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Mineralogical and geochemical trends of the Vaca Muerta-Quintuco system in the Puerta Curaco section, Neuquén Basin

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ABSTRACT

The deposits of the Vaca Muerta-Quintuco system (Tithonian-Valanginian) have been analyzed in the Puerta Curaco section to study the mineralogical and geochemical variations through the progressive transition from a carbonate ramp (Vaca Muerta Formation) to a mixed shelf (Quintuco Formation). A lithostratigraphic log, gamma-ray measurements (GR), mineralogical (XRD) and geochemical analysis (XRF) allowed to define five intervals: I1-I5. I1 and I2 belong to the Vaca Muerta Formation. They are dominated by carbonate sedimentation and present the highest values of organic proxies of the system. The total GR values are strongly dependent of the U content and the V/V+Ni ratio suggests alternating anoxic and euxinic conditions of the sea bottom. I3 is developed in the transition between both units and exhibits a sudden increase in the clay mineral content and a decrease in the organic proxies, associated to a sea level fall. I4 and I5 belong to the Quintuco Formation. I4 is characterized by a renewed increase in the carbonate sedimentation while I5 records the highest clastic input to the basin, evidencing the settling of the mixed shelf. In the Quintuco Formation, the V/V+Ni ratio suggests anoxia/dysoxia at the sea-bottom. In addition, a decrease in the organic proxies and an excellent correlation between total GR and K and Th is recorded. Decreasing organic matter content in the Quintuco Formation is attributed to a dilution phenomenon caused by the increasing detrital input and not by changes in the oxygenation of the sea-bottom.

Palabras clave: *geochemistry, organic matter, shale, sequence stratigraphy, paleoenvironmental analysis*

RESUMEN

Tendencias mineralógicas y geoquímicas del sistema Vaca Muerta-Quintuco en la sección de Puerta Curaco, Cuenca Neuquina.
Se estudiaron los depósitos del sistema Vaca Muerta-Quintuco (Tithoniano-Valanginiano) en la localidad de Puerta Curaco con el objetivo de analizar las variaciones mineralógicas y geoquímicas de la transición desde una rampa carbonática (Formación Vaca Muerta) a una plataforma mixta (Formación Quintuco). Para ello, se realizaron un perfil litoestratigráfico, mediciones de radioactividad natural (GR), estudios mineralógicos (DRX) y geoquímicos (FRX), definiendo cinco intervalos: I1-I5. I1 e I2 se desarrollan en la Formación Vaca Muerta, se encuentran dominados por sedimentación carbonática y presentan los mayores valores de *proxies* orgánicos del sistema. La respuesta del GR se relaciona directamente con el contenido de U y la relación V/V+Ni sugiere una alternancia entre condiciones euxínicas a anóxicas del fondo marino. I3 se desarrolla en la transición entre ambas unidades, presenta un aumento brusco en el contenido de minerales arcillosos y una disminución de *proxies* orgánicos, asociándose a un descenso del nivel del mar. I4 e I5 se desarrollan en la Formación Quintuco. I4 se encuentra dominada por sedimentación carbonática, mientras que I5 registra los mayores valores de input clástico, evidenciando el establecimiento de la plataforma mixta. En la Formación Quintuco, la relación V/V+Ni sugiere condiciones de anoxia/disoxia, registrándose una notoria disminución en los *proxies* orgánicos y una fuerte dependencia del GR con el K y Th. Por lo tanto, la disminución en el contenido orgánico de la Formación Quintuco es causada por la dilución debida al mayor aporte de detritos inorgánicos y no por cambios en la oxigenación del fondo marino.

Keywords: *geoquímica, materia orgánica, shale, estratigrafía secuencial, análisis paleoambiental*

INTRODUCTION

The Vaca Muerta-Quintuco system (Tithonian-Valanginian) has received worldwide attention during the last decade, since the Vaca Muerta Formation represents the most effective source rock of the Neuquén Basin (Uliana and Legarreta 1993) and is considered as a world-class unconventional oil and gas play (Askenazi *et al.* 2013 and references therein). Although considerable work has been done regarding the main sedimentological, stratigraphical and paleontological aspects of both units in many locations of the basin, so far there is neither a study of the general mineralogical and geochemical trends nor an agreement on the stratigraphic position of the boundary between the Vaca Muerta and Quintuco Formations in the northern area of the Neuquén Basin, mainly because it is difficult to discriminate both units in distal positions of the basin (Leanza *et al.* 2011). The Quintuco Formation has been subdivided into carbonate-rich (Tithonian-Berriasian) and mixed siliciclastic-carbonate (Berriasian-Valanginian) facies (Olmos *et al.* 2002). On the Chos Malal fold and thrust belt, Kietzmann *et al.* (2016a) have established the boundary between Vaca Muerta and Quintuco Formations after a decrease of total organic carbon (TOC) and calcite content, with an important increase of clay minerals and detrital material, along with the occurrence of dolomitized levels.

The Puerta Curaco section is a well-known outcrop of the northern part of the basin since the work of Weaver (1931). It shows a well exposed section in which the Vaca Muerta Formation passes transitionally to the Quintuco Formation. The sediments in the transition interval are mostly composed of fine-grained, black or gray marlstones, limestones/dolostones and mudstones and show similar appearance. Subtle sedimentological, mineralogical and geochemical changes reflect the well-known decrease in organic matter content in the Quintuco Formation (*e.g.*, Uliana and Legarreta 1993, Stinco and Mosquera 2003, Uliana *et al.* 2014, Fantín *et al.* 2014, González Tomassini *et al.* 2015, Kietzmann *et al.* 2016a) and the marked facies change that take place in shallower, proximal parts of the basin (Carozzi *et al.* 1993, Olmos *et al.* 2002). Therefore, this section is ideal to analyze the changes underwent in a deeper part of the basin and to discuss the position, sequence-stratigraphic and paleoenvironmental meaning of the transition between Vaca Muerta and Quintuco Formations. We use mineralogical and geochemical proxies, as well as gamma-ray measurements in order to characterize that transition, hoping this would be useful in the oil industry, since it may serve as a reliable reference for correlation in subsurface operations, when information is limited to electrical logs, cuttings or stratigraphic-selected cores.

The aim of the present contribution is to define the main geochemical trends of the Vaca Muerta-Quintuco system, to analyze the transition between both units as well as to characterize and discuss the main sedimentological and paleoenvironmental aspects in the Puerta Curaco section.

GEOLOGICAL SETTING: STRUCTURE AND STRATIGRAPHY

Overview of the tectonic evolution of the Neuquén Basin

The Neuquén Basin, western Argentina (Fig. 1a), is a Mesozoic-Cenozoic oil- and gas- productive basin, with a sedimentary column up to 7000 m thick. The formation of the basin started with a rifting process that lasted from the Late Triassic to the Early Jurassic. The basin was submitted to important thermal subsidence (Mitchum and Uliana 1985, Legarreta and Gulisano 1989) and changed to a back-arc basin during the Early Jurassic-Early Cretaceous. A volcanic arc was progressively developed to the west and the basin was periodically flooded by the paleo-Pacific Ocean (*e.g.*, Legarreta and Uliana 1991). During the late Tithonian-early Berriasian a marine transgression generated the deposits of the Vaca Muerta and Quintuco Formations included in the Mendoza Group (*e.g.*, Mitchum and Uliana 1985, Legarreta and Gulisano 1989, Spalletti *et al.* 2015). Finally, during the Late Cretaceous-Cenozoic, the Neuquén Basin underwent the compressive regimen of the Andes orogeny. The flexural subsidence generated a fold-and-thrust-belt with a foreland basin to the east (Ramos 1999, Howell *et al.* 2005)

Structure and stratigraphy of the Puerta Curaco section

The Puerta Curaco section is located 30 km eastern of the Chos Malal town (Fig. 1b) in the northern part of the Neuquén province. It is at the southern tip of the south-verging La Yesera anticline (Fig. 1c), which is part of a series of N-S striking anticlines, probably generated from slips with east vergence (Kozlowski *et al.* 1996, Guzman *et al.* 2011). They are characteristic of the thin-skinned Chos Malal fold-and-thrust-belt, which was formed during the Andes orogeny on a succession of Mesozoic strata (Sánchez *et al.* 2015).

The late Kimmerdigian-Barremian stratigraphic record in Puerta Curaco area includes the Auquilco, Tordillo, Vaca Muerta, Quintuco, Mulichinco and Agrio Formations (Leanza and Hugo 1977). The Vaca Muerta-Quintuco system crops out in the eastern limb of La Yesera anticline (Fig. 1b) with a total thickness of 716 m. It concordantly overlies the fluvial, green siltstones of the Tordillo Formation (Spalletti and Veiga 2007) and is concordantly covered by the heterolithic sandstones and mudstones of the Mulichinco Formation, accumulated in a tide- and wave-influenced shelf with common storms deposits (Schwarz 1999).

The Vaca Muerta-Quintuco system

Weaver (1931) firstly described the rocks of the Vaca Muerta Formation naming them “Tithonian marine strata” (Vaca Muerta Formation in plate 1), characterized by sandy mudstones with interbedded limestones and sandstones up to 200 m thick in the southern part of the basin (southern Neuquén Province) and by black calcareous mudstones up to 800 m thick in the northern part of the basin (in central/northern Neuquén and Mendoza Provinces). Weaver concluded that the Tithonian strata were deposited under shallow to moderate water depth in the southern part of the basin, and under moderate water depth in a slowly submerging embayment, in the northern part of the basin. Weaver (1931) gave the name Quintuco Formation to the Lower Cretaceous marine sediments of the Neuquén Province, which are constituted by dark grey to black mudstones, more calcareous and sandy

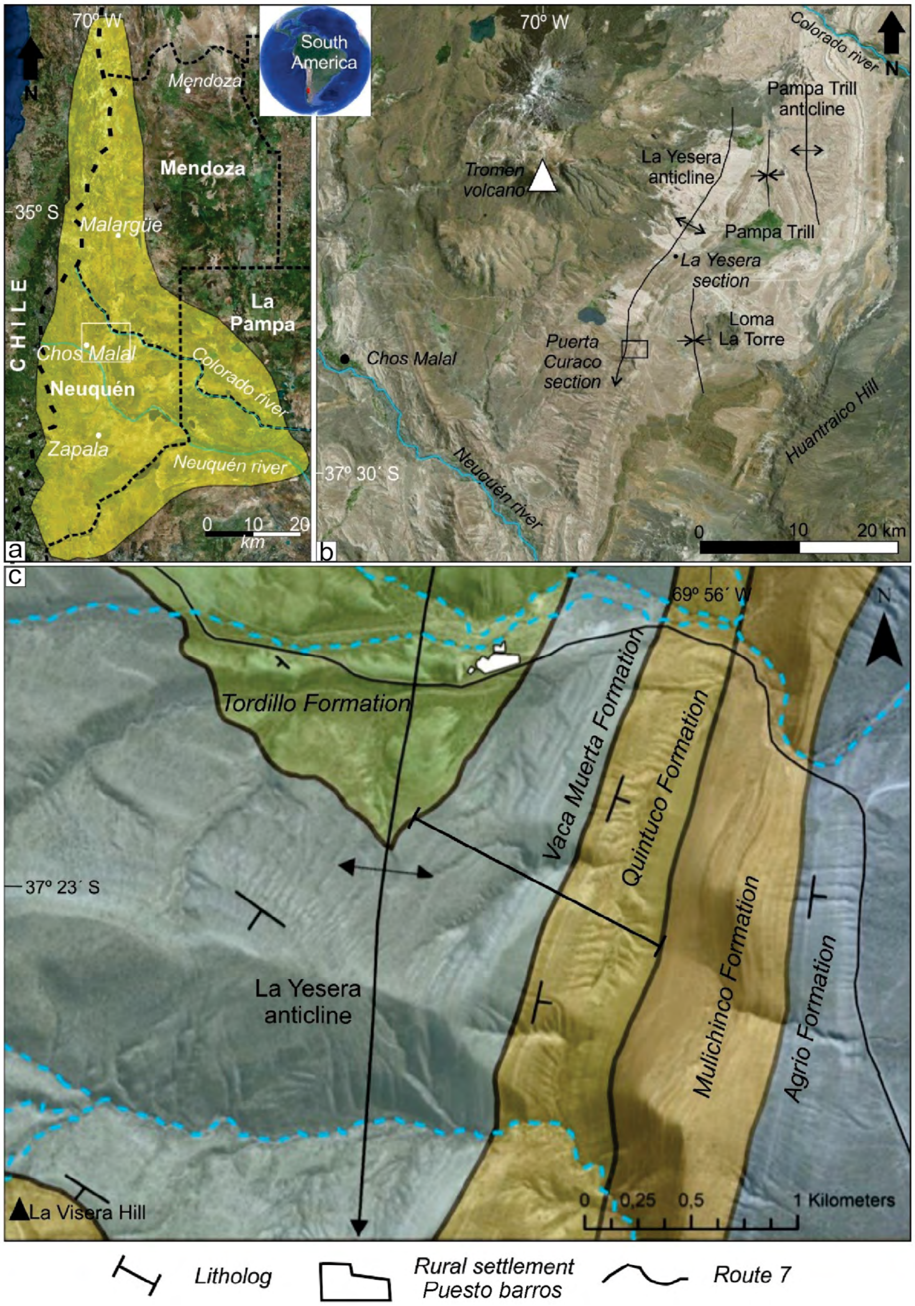

Figure 1. a) Geographic location of the Neuquén Basin, western Argentina. b) Location of the Puerta Curaco section on the eastern limb of La Yesera anticline. c) Geological sketch map of the La Yesera Anticline.

to the south. Because the rocks of the Vaca Muerta and Quintuco Formations are similar in the northern, depocentral areas, Leanza (1973) incorporated them in the Vaca Muerta Formation.

The Vaca Muerta-Quintuco marine system overlies the fluvial Tordillo Formation. This contact is easily recognized on the entire basin, since it evidences a regional retrogradation pattern in response to a marine transgression from the paleo-Pacific Ocean (Legarreta and Gulisano 1989). In the northern Neuquén basin the Vaca Muerta Formation begins with a characteristic microbial level (Kietzmann *et al.* 2014a,b, 2016a,b). The Intravalanginian unconformity separates the system from the overlying shelf deposits of the Mulichinco Formation (Valanginian). However, in distal positions of the basin, this contact is regarded as concordant and interpreted as a “relative conformity” in sequence stratigraphic terms (see Leanza *et al.* 2011 and references therein). The Vaca Muerta-Quintuco system is characterized by a series of SE-NW or S-N prograding clinoforms (Mitchum and Uliana 1985). The shallow-water deposits in the topsets of the the clinoforms accumulated in mixed siliciclastic-carbonate shelfs whereas the deposits in the bottomset correspond to outer ramp/basin environments (Mitchum and Uliana 1985, Spalletti *et al.* 2000, Scasso *et al.* 2005, Kietzmann *et al.* 2014b, 2016a). Due to the high organic content, slope and basinal positions (bottomset) are prone to be the best unconventional targets (Mitchum and Uliana 1985, Desjardins *et al.* 2016).

Previous stratigraphic studies in the Puerta Curaco area

After the work of Weaver (1931), sequence-stratigraphic and paleontological studies on the Vaca Muerta-Quintuco system were carried out by Mitchum and Uliana (1985) in several localities, including Puerta Curaco area. Previously, Leanza and Hugo (1977) measured a total thickness of 325,5 m for the Vaca Muerta Formation (including the Quintuco Formation) and of 370 m for the overlying Mulichinco Formation, suggesting an early Tithonian-early Valanginian age for the system. The Vaca Muerta-Quintuco system in Puerta Curaco area has been interpreted as a shallowing upward system, characterized by the outer ramp/basin deposits of the Vaca Muerta Formation, covered by the slope/basin to offshore/transition deposits of the Quintuco Formation (Mitchum and Uliana 1985, D´Odorico 2009, Legarreta 2009, Kietzmann *et al.* 2014c, Kietzmann *et al.* 2016). Recently, Kietzmann *et al.* (2016a) have identified 5 composite sequences (CS) and 15 high-ordered sequences (HFS), with a general distribution of TOC, calcite, clays and detrital input. Weger *et al.* (2017) performed a sequence stratigraphic and organic carbon distribution analysis on the Vaca Muerta Formation. In La Yesera section, 11 km to the north of Puerta Curaco (Fig. 1b) detailed facies analysis and paleontological observations on the Vaca Muerta Formation were done by Spalletti *et al.* (1999), whereas the sedimentology of Quintuco and lower Mulichinco Formations was studied by Schwarz *et al.* (2011).

MATERIAL AND METHODS

Fieldwork, litholog and sampling

A detailed litholog was performed on the entire Vaca Muerta-Quintuco system (716 m). Thickness was measured bed by bed with a Jacob´s staff. Stacking patterns were used to recognize composite sequences (CS), subdivided into high-frequency sequences (HFS) and very-high-frequency sequences (or parasequences). Sequences were subdivided into a transgressive system tract (TST) and a regressive system tract (RST) (*e.g.*, Embry and Johannessen 1992). Almost 70 samples were collected with a sampling interval about 15 m. The sampling interval was reduced to 0,5 m within the Vaca Muerta-Quintuco transition interval. Mudstones, marlstones, calcareous marlstones and limestones were distinguished with field criteria as more calcareous strata are more resistant to weathering. Calcareous content in mudstones was also estimated with HCl.

Inorganic Geochemistry

Gamma-ray measurements: Spectral gamma-ray radioactivity was measured every 0,5 or 1 m using a RS 230 GammaRay Spectrometer. Individual measurements lasted 120 seconds on the first 483 m of the system. The concentration of each radioelement (K, U and Th) was determined with the equation: $n_i = S_{iK}C_K + S_{iU}+C_U + S_{iTh}C_{Th}+n_{iBG}$, where n represents the count rate in the energy window, S_i sensitivity of the spectrometer for the detection of the element, C the concentration of the element (% K, ppm U, ppm Th) and n_{iBG} the background count rate (IAEA 2003). Authigenic U contribution was calculated with the equation $U_{authigenic} = U_{total}$ - Th/3 following Wignall and Myers (1988). The last 233 m of the outcrop (upper part of the Quintuco Formation) were measured with SGR every 10 m, whereas total gamma-ray (GR) measurements were done every 1 m with a portable Gamma-Ray radiometer E076-A0 (premarket prototype by CNEA).

X-Ray Fluorescence analysis: A Niton XL3t Ultra Analyzer was used for determining major and minor elements (Si, Al, K, Ca, Fe, S, Ti and P) and trace elements (Zr, Sr, Mo, V, Ni, Zn, Cu) in the lab. Na and Mg were excluded of the analysis because the low accuracy of the measurements. Measurements lasted 90 seconds and internal standards were measured periodically to check reproducibility. Almost 70 marlstones and mudstones were studied in Vaca Muerta and Quintuco Formations to determine vertical geochemical variations. V/(V+Ni) ratio was used to characterize the paleoredox conditions of the environment (Hatch and Leventhal 1992). A cut-off value of 25% CaO was used to discriminate marlstones and mudstones from limestones. Limestones were excluded from the analysis because the high content of CaO and CO_2 produces a high dilution of the trace-element abundance within the sample, masking the main trends in the column (*e.g.*, Tribovillard *et al.* 2006).

Mineralogy

Microscope analysis: 100 thin sections of marlstones, limestones and mudstones were analyzed under the polarizing microscope to define microfacies, and to characterize and contrast the main textural features between Vaca Muerta and Quintuco Formations.

X-Ray diffraction: Both bulk and clay mineralogy (< 2 μm) were analyzed from Vaca Muerta Formation marlstones and Quintuco Formation calcareous mudstones using a Phillips X-Pert PW3710 and a Bruker D2 Phaser equipments (CETMIC, Argentina). Rocks were firstly gently disaggregated with an agatha mortar and then, randomly oriented powdered sampled were scanned from 3-70°, with a step size of 0,04 2θ°. To obtain the clay-mineral fraction, carbonate was removed using a sodium acetate-acetic acid buffer solution (Jackson 1969). Once the solution was carbonate-free, organic matter was removed using hydrogen peroxide (Moore and Reynolds 1997). Three oriented clay aggregates, air-dried (AD), ethylene-glycol solvated (EG) and heated (H) to 550°C for 2 hours, were studied. Identification of the clay mineralogy was done after the position of their basal reflections between 2-32° following Moore and Reynolds (1997). To analyze vertical mineralogical variations through the system semi-quantitative determinations of quartz, calcite, plagioclase and clay-minerals were done accordingly to the area of the main peak (100% intensity) except for quartz (the 4.2Å peak of 21 % intensity) and total clays (the 4.5Å peak of 53 % intensity). Correction factors of 5 and 2 were respectively applied for the measured surfaces of quartz and total clays (*e.g.*, Xu *et al.* 2017).

RESULTS

Litholog and sequence stratigraphy

The Vaca Muerta Formation is formed by a 407 m thick, marlstone/limestone rhythmic succession (Figs. 2a, 6) and both argilized (Fig. 2b) and calcitized tuffs are intercalated. Sub-spherical carbonate concretions (Fig. 2c), with an average diameter of 10 cm, are common in some beds, as well as interbedded beef-veins (*e.g.*, Rodriguez *et al.* 2009) averaging 1 cm thick (Fig. 2d). 2-7 cm thick microbial laminated bindstones (B_ml - Kietzmann *et al.* 2016a,b) are commonly observed (Fig. 2e).

The Vaca Muerta Formation comprises four entire CS, as well as the TST of the 5th CS (Fig. 8). Thickness of the CS may vary from 50 (CS1) to 112 m (CS2). TSTs are richer in carbonate concretions and are usually characterized by the presence of B_ml. The B_ml are usually located at the lowermost part of the TSTs and have been interpreted as a marker of the sequence boundaries (Kietzmann *et al.* 2016a). TSTs are characterized by a higher marlstone/limestone ratio, whereas the opposite is true for the RSTs, which is characterized by a progressive increasing on the carbonate content towards the top of the sequence (Kietzmann *et al.* 2016a). This stacking pattern is also observed on the 13 HFSs described for the Vaca Muerta Formation. The thickness of the HFS varies from 12 to 50 m.

The contact between Vaca Muerta and Quintuco Formations has been set in the lower dolostone bed (407 m from the base of the Vaca Muerta Formation), following lithostratigraphic criteria (Fig. 6). The Quintuco Formation is 309 m thick and has been subdivided into two members (Fig. 6): 1) The Puesto Barros Member (PBMb) which comprises the lower 76 m, composed of mudstones, calcareous mudstones, limestones and dolostones. Five tabular, orange-colored dolostone beds are prominent in the lower 30 m of the member (Fig. 2f), which characterizes the transition interval between both units. 2) The Cerro La Visera Member (CVMb), with a total thickness of 233 m. The Cerro La Visera Member is characterized by a succession of mudstones and calcareous mudstones (Fig. 2g), with rare limestones, fine-grained sandstones and bioclastic sandstones. The sandstone/mudstone ratio is markedly low in the base of the member, and trends to increase towards the top of the unit, as well as the bioclastic content. In the last 80 m of the Cerro La Visera Member, tabular and columnar dolomite concretions are found (Fig. 2h).

The Quintuco Formation comprises the RST of the CS 5. A correlative conformity surface, correlated to the Intravalanginian unconformity (Gulisano *et al.* 1984, Leanza 2009), separates it from the overlying Mulichinco Formation. The Quintuco Formation is subdivided into three HFS (50 to 118 m thick), with TSTs characterized by carbonate facies and RSTs enriched in mudstones (Kietzmann *et al.* 2016a). The four parasequences of the HFS-16 have similar arrangements of their system tracts.

A transition interval (42 m) encompassing the last 7 m of the Vaca Muerta Formation and the basal 35 m of Puesto Barros Member is defined here. This interval is characterized by the presence of black, laminated mudstones, interbedded dolostones and beef veins (Fig. 2f). The mudstone:dolostone ratio is 30:1. Calcitized and argilized tuffs are rare.

Petrographic analysis

Microfacies analysis of the Vaca Muerta and Quintuco Formations in the Puerta Curaco area reveals a wide range of sedimentary and diagenetic processes that are essential for the understanding of this heterogeneous unconventional shale system (*e.g.*, Kietzmann *et al.* 2014c, Kietzmann *et al.* 2016a,b). The Vaca Muerta Formation contain a mixture of components of different origins, including epiclastic, carbonate, and volcaniclastic particles, where dominant microfacies are related to accumulation of sand-size mud-intraclasts, and a low proportion of terrigenous particles and clays. By contrast the Quintuco Formation consists mostly of epiclastic components with subordinated carbonates, indicating a mayor paleoenvironment change (Kietzmann *et al.* 2016a).

Vaca Muerta Formation: The main microfacies includes laminated mudstones/marlstones (Fl/Mrh), microbial bindstones (B_ml), radiolaritic wackestones (W_rh), intraclastic packstone/grainstone (PG_ih), bioclastic wackestones/packstones (WP_bh), massive to laminated calcite-replaced tuff (Tch, Tcm), massive to laminated clay-altered tuff (Tah, Tam), and calcite-replaced lapillite (Lm, Lg).

- Laminated mudstones/marlstones (Fl, Mrh) consist of black to dark gray, laminated mudstones/marlstones with abundant organic matter. It is one of the most abundant microfacies in Vaca Muerta Formation. Particles include silt-sized quartz and plagioclase clasts, bivalves and ammonite fragments, as well as scarce calcitized radiolaria (Fig. 3a). The matrix consists of fine silt-sized quartz and plagioclase grains, bioclastic debris, and coccolith fragments. Cements include microgranular quartz, and granular calcite.
- Microbial bindstones (B_ml) consist of thinly laminated, fine-grained limestones, rich in organic matter with minor silt-sized clasts and clays. The most evident feature is the conspicuous submillimeter-to millimeter-scale horizontal to sub-horizontal lamination (Fig. 3b). Grains consist of thinly shelled oysters, ammonite and fish remains, and radiolarians. Silt-sized quartz and plagioclase clasts also occur in low proportions.
- Radiolaritic wackestones (W_rh) are well laminated, dark grey to black in color, and contain abundant radiolarians, benthic foraminifera, *Saccocoma*, ammonites, transported infaunal bivalves (Fig. 3c). Terrigenous clasts occur in low proportions (<10%) and include silt-sized quartz, plagioclase and feldspar.
- Intraclastic packstone/grainstone (PG_ih) is one of the most abundant microfacies in Vaca Muerta Formation. It shows typically horizontal lamination, and dominant particles are well sorted, subangular to angular, fine to medium sand size micritic intraclasts (Fig. 3d). Fossil content include radiolarian, benthic foraminifera, ammonites, articulated and disarticulated bivalves, and gastropods. Terrigenous clasts occur in low proportions (<10%) and include silt-sized quartz, plagioclase and feldspar.
- Bioclastic wackestones/packstones (WP_bh) are dark grey to brown and typically massive or laminated. They contain abundant disarticulated and fragmented bivalves, including oysters, infaunal aragonitic bivalves, gastropods and ammonite fragments. Other bioclasts include benthic foraminifera, *Saccocoma*, and occasionally serpulids. Terrigenous clasts are also low within this microfacies.
- Massive to laminated, calcite-replaced tuffs (T_ch, T_cm) forming tabular carbonates beds of crystalline appearance. They are usually massive, laminated, or have ripple lamination. They are composed of abundant glass shards and pumiceous fragments immerse in a poikilotopic calcite cement (Fig. 3e). Glass shards and pumiceous fragments are partially altered to clay minerals.
- Clay-altered tuff deposits (T_ah, T_am) occur as tabular argillaceous beds, usually very weathered. They consist of glass shards and pumiceous fragments completely altered to clay minerals. Silt-sized plagioclase grains and disperse pyrite are also common.
- Lapillite (Lm, Lg) deposits are massive or inverse graded. They are composed of coarse sand to granule-sized pumiceous fragments, mostly replaced by calcite (Fig. 3f). They usually have a micritic matrix, and contain other particles like crustacean pellets, bivalves, and radiolarians.

Quintuco Formation: Typical microfacies of the Quintuco Formation include laminated mudstones (Fl), dolostones (D), terrigenous wackestones (W_th), bioclastic floatstones/rudstones (FR_bm), and laminated sandstones (Sh).

- Laminated mudstones (Fl) in the Quintuco Formation are gray to light gray. Particles are dominated by silt-to-mud-sized quartz, feldspar, and plagioclase, and subordinately scarce radiolarians and bioclastic detritus. The matrix is composed by argillaceous components, showing a significant increase in clay minerals with respect to the Vaca Muerta Formation.
- Dolostones (D) are horizontaly laminated and laterally continuous, dolomitized beds, although they can be also developed as horizons with brecciated dolomite septarian concretions. They have a

Figure 2. Main lithologic features of Vaca Muerta and Quintuco Formations in the study area.
a) Typical marlstone/limestone succession of Vaca Muerta Formation. b) Whitish, argillaceous tuffs intercalated with dark gray marlstones of Vaca Muerta Fm. c) Sub-spherical carbonate concretions developed in the marlstones of the Vaca Muerta Formation d) Fibrous beef-vein within brown calcareous marlstones. Beef veins may present black bituminous layers in the center. e) Laminated microbial bindstone of the Vaca Muerta Formation, usually observed at the base of the TSTs. f) Dolostone bed at the base of the Quintuco Formation in the transition interval (Puesto Barros Mb.). Note the laminated black mudstones surrounding the dolomitic level. g) Succession of fine-grained sandstones with calcareous mudstones in the Cerro La Visera Mb. h) Columnar dolomitic concretions developed within calcareous mudstones in the Cerro La Visera Mb.

characteristic orange color in the Puesto Barros Member. In thin section this microfacies is characterized by an equigranular mosaic of anhedral to subhedral crystals, containing isolated terrigenous clasts and calcispheres (Fig. 4a).

- Terrigenous wackestones (W_th) are typically laminated and their tops are generally bioturbated. This microfacies occurs mostly in the Puesto Barros Member. Particles include small disarticulated ostracods, ophiuroid ossicles, and occasionally benthic foraminifera (*Lenticulina* sp. and *Nodosaria* sp.). Terrigenous grains are much abundant than in the other limestones, reaching up to 30% of the total volume. Clasts include coarse silt-to fine sand-sized quartz and plagioclase as major components, together with muscovite and more rarely biotite. (Fig. 4b).

- Bioclastic floatstones/rudstones (FR_bm) forming massive or normally-graded beds. Particles include oysters, altered aragonitic bivalves, serpulids, echinoderms, benthic foraminifera, sponge spicules, and silt-to fine sand-sized terrigenous clasts (quartz, plagioclase and feldspars). Matrix is commonly peloidal (Fig. 4c).

- Horizontally laminated to ripple laminated sandstones (Sh, Sr) are feldarenites and volcanic lithoarenites. They are composed of medium to fine sand-sized volcanic and sedimentary lithic fragments, plagioclase, feldspar, micas, and monocrystalline quartz. Clasts are subangular. Isolated, rounded clasts of phosphate and glauconite are common. The interparticular space is filled with micrite or granular calcite cement (Fig. 4d).

Mineralogical analysis: X-Ray Diffraction (XRD)

Bulk-rock minerals: The Vaca Muerta-Quintuco system is characterized by an homogenous, non-clay mineralogy. The main constituents are quartz and calcite, with subordinated plagioclase (Figs. 5, 6). Gypsum, pyrite, and carbonate-fluorapatite were recorded in specific intervals as trace minerals within the Vaca Muerta Formation and on the Puesto Barros Member (Fig. 6). Total clay content is very low within the Vaca Muerta Formation marlstones (Figs. 5, 6) and progressively increases towards the top of the Quintuco Formation. The clay minerals/calcite ratio is considerably low within the Vaca Muerta Formation, with a remarkable increase in the transition interval and in the last 150 m of the Cerro La Visera Member.

The dolostone beds developed in the transition interval (Fig. 2f, 4a) are formed by dolomite (83-95 %), with low contribution of calcite (1-7 %), quartz (2-6 %), plagioclase (2-3 %) and clay minerals (<1 %) (Scasso *et al.* 2017).

Clay-minerals: The clay mineralogy of the marlstones of Vaca Muerta Formation is dominated by mixed-layer I/S (Fig. 7a), with occasional chlorite as a trace mineral (Capelli *et al.* 2017a, b). The mixed-layer I/S is classified as a R3 (Moore and

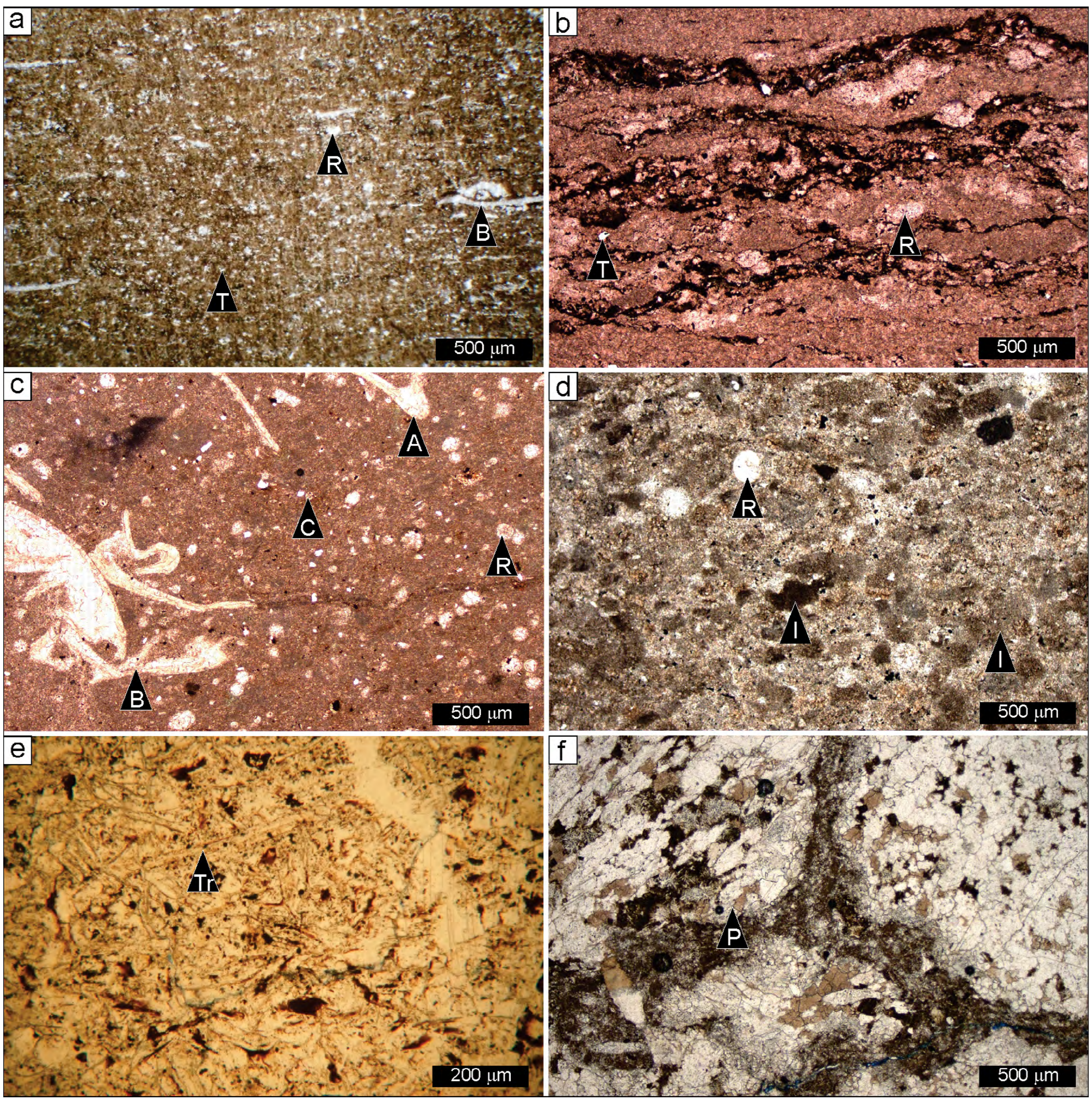

Figure 3. Main microfacies of the Vaca Muerta Formation at Puerta Curaco: a) Laminated mudstones, showing fragments of bivalves (B), radiolarian (R) and terrigens (T); b) Microbial bindstones showing a characteristic alternation of micritic and microsparitic laminae, that include radiolarian (R), terrigenous (T) and other microfossils; c) Radiolaritic wackestones showing a radiolarian (R), calcispheres (C), and fragments of bivalves (B) and ammonites (A); d) Intraclastic packstone/grainstone forming a grain-supported fabric from the accumulation of intraclasts (I) and radiolarian (R); e) Calcite-replaced tuff, showing abundant glass shards (Tr) partially altered to clays; f) Calcite-replaced lapillite which consists of the accumulation of pumiceous fragments (P) in a micritic matrix.

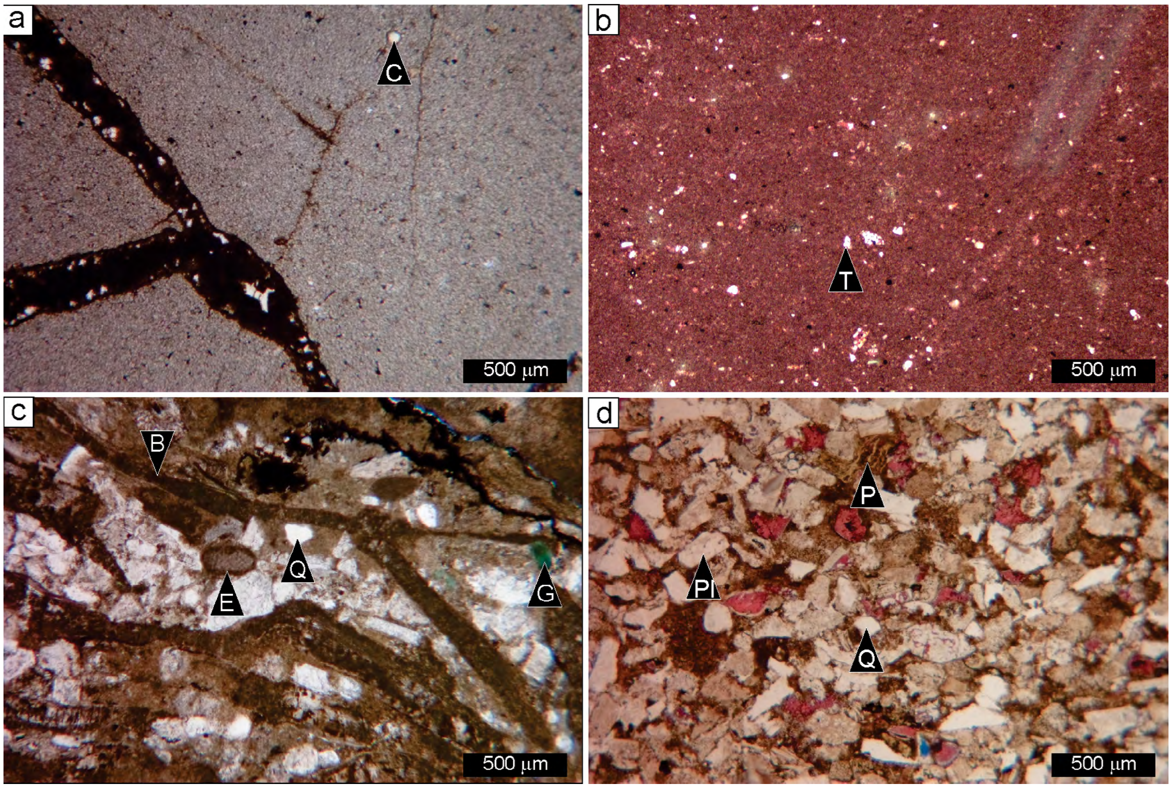

Figure 4. Main microfacies of the Quintuco Formation at Puerta Curaco: a) Dolostone from the Puesto Barros Member showing a characteristic subhedral crystalline fabric among which some remains of the primary components, such as calcispheres (C), are observed; b) Wackestone with terrigenous clasts from the Puesto Barros Member, showing terrigenous clasts (T) within a mud-supported micritic matrix; c) Bioclastic rudstone from Cerro La Visera Member with fragments of bivalves (B), echinoderms forming cortoids (E), terrigenous (Q) and glauconite (G); d) Lithoarenite from Cerro La Visera Member, showing pumiceous fragments (P), plagioclase (Pl) and quartz (Q) and micritic intraclasts.

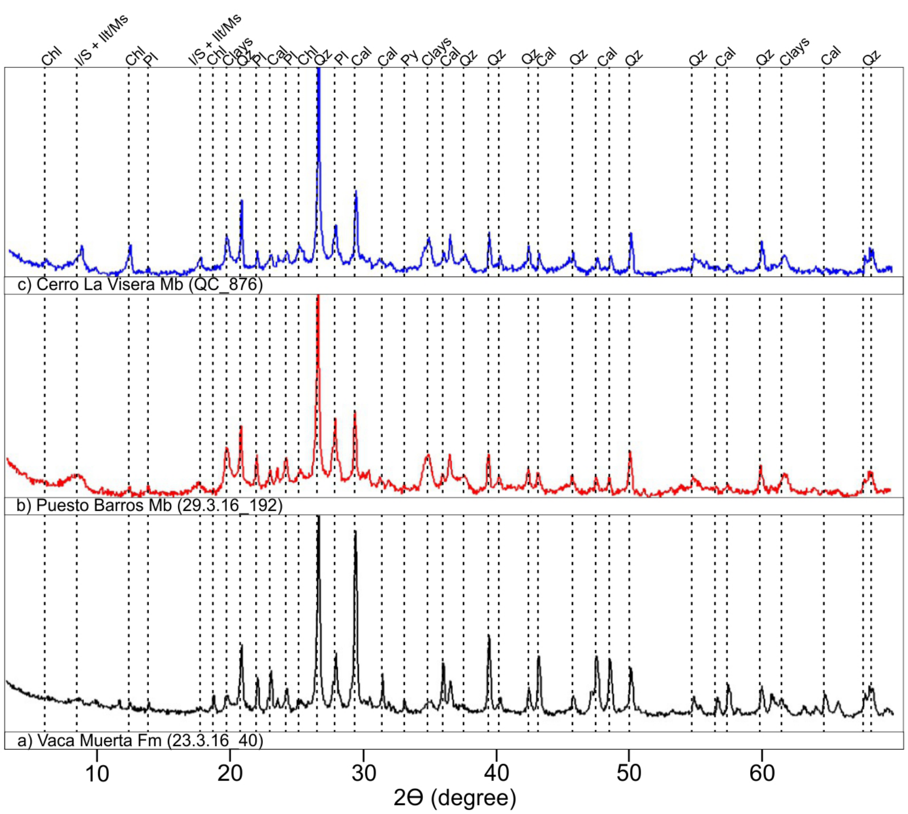

Figure 5. Bulk rock typical XRD patterns. a) Marlstone of the Vaca Muerta Formation. b) Calcareous mudstone of the PBMb. c) Calcareous mudstone of the CVMb. The non-clay minerals, quartz, calcite and plagioclase present variable contribution. The clay mineral content is low in Vaca Muerta Formation and increases in both members of the Quintuco Formation. Abbreviations (IMA): Chl: chlorite, I/S: mixed-layer illite/smectite, Ilt: illite, Ms: muscovite, Pl: plagioclase, Qz: quartz, Cal: calcite, Py: pyrite.

Reynolds 1997), since the expandable layers represent less than de 10% of the mixed-layers. Considerable contribution of fine-grained quartz has been recorded in the clay mineral fraction, especially in Vaca Muerta marlstones (Fig. 7a). The transition interval is characterized by the presence of chlorite, mixed-layered I/S and illite. The chlorite pattern presents an important asymmetry on the reflections, with strong reflections on the even peaks and weak reflections on the odd peaks (Fig. 7b), indicating an Fe-rich chlorite (Moore and Reynolds 1997). The illite contribution is differentiated from the I/S, recorded on narrower peaks in the 10 and 5 Å positions (Fig. 7b). Finally, the Cerro La Visera Member (Fig. 7c) is dominated by illite, with a subtle contribution of I/S generating an asymmetry the 10Å peak. Chlorite is also observed within the Cerro La Visera Member with poorly developed odd peaks, as previously described for the transition interval (Fig. 7c).

Inorganic Geochemistry Gamma-Ray spectroscopy

Six intervals with high total GR values are recorded within the Vaca Muerta Formation (Fig. 8). The thickness of these intervals varies between 9 and 48 m (Fig. 8). They are linked to high values of U (Fig. 8), which may reach up to 21 ppm, and are usually located on the TSTs on both CS and HFS. K and Th contribution is relatively low and stable throughout the Vaca Muerta Formation. Nevertheless, a subtle increasing trend is observed from the end of the TST of CS 2 (maximum flooding surface) to the top of the unit (Fig. 8). When analyzing the authigenic vs detrital contribution of U (Wignall and Myers 1988) for the Vaca Muerta Formation, it is observed that the U contribution is mostly of authigenic origin, with a negligible detrital contribution (Fig. 8).

On the other hand, the Quintuco Formation records 6 anomalies of total GR (Fig. 8), varying between 10 to 73 m thick. They usually correspond to the RST of the HFS and to the RST of the parasequences in the upper 85 m of the formation. Opposite to the Vaca Muerta Formation, the GR anomalies correlate to high values of K and Th and the U is mainly of detrital origin (Fig. 8).

The anomaly of the transition interval between the Vaca Muerta and Quintuco Formations (Fig. 8) present higher contribution of K and Th, whereas U values are remarkably low and mainly of detrital origin. The total GR correlates well to the U spectrum in the Vaca Muerta Formation, whereas no correlation is observed in the Quintuco Formation (Fig. 9a). The opposite is observed for K (Fig. 9b).

Major and trace elements

The elements were grouped according to their affinity (Calvert and Pedersen 2007, Montero-Serrano *et al.* 2010, 2015). Main elements of the siliciclastic, carbonate, organic and sulfide groups were plotted in figures 11 and 12.

Siliciclastic group: Si, Al, K, Ti and Zr are typically representative of this group. They are usually associated with clay, silt and sand particles, either as the main chemical constituents of the detrital grains (*e.g.*, quartz, K-feldspar) or adsorbed on their surface (see Calvert and Pedersen 2007, Montero-Serrano *et al.* 2010, 2015). Si is associated to quartz. As quartz may or may not present a detrital origin, Si vs Zr correlation helps to unravel its origin (*e.g.*, Calvert *et al.* 1996, Ross and Bustin 2009, Dowey and Taylor 2017) (Fig. 10). Si (14-32 %) is the most abundant element of this group. It shows relatively homogeneous values throughout the section (Fig. 11). Al and K values are variable within the first 190 m (T5) of the Vaca Muerta Formation. Afterwards, a general increasing tendency is observed towards the base of Mulichinco Formation, reaching maximum values on the upper 150 m of the Cerro La Visera Member (Fig. 11). The transition interval is characterized by an important increase on both elements as well as in Ti, which shows a similar behavior to K and Al (Fig. 11).

Carbonate group: Ca and Sr are selected for the analysis. Ca content is highly variable in the entire system, with a minimum value of 1 % and a maximum of 25 % (Fig. 11). Despite local variations, the transition interval is characterized by lower contents of Ca, as well as the last 150 m of Cerro La Visera Member (Fig. 11). Sr/Ca ratio shows a steady increase from base to top of the system, with remarkably high Sr values in the upper 150 m of Cerro La Visera Member. The transition interval records a subtle increase in the Sr/Ca ratio (Fig. 11).

Organic group: P, Mo, Ni and V, represent the elements with high affinity to the organic matter (*e.g.*, Algeo and Maynard 2004, Tribovillard *et al.* 2006). Mo, Ni and V contents are characterized by an important variability within the first 200 m of the Vaca Muerta Formation, where they reach the highest values: 363, 334 and 1047 ppm respectively (Fig. 12). Then, a general decreasing tendency is observed in these elements towards the top of the Vaca Muerta Formation. They are notably depleted in the transition interval, a tendency that continues upwards in the Quintuco Formation (Fig. 12). Mo is below the detection limit in specific samples within the transition interval and on the upper 150 m of Cerro La Visera Member (Fig. 12). P content is markedly low and is beneath the lower detection limit in 9 samples (Fig. 12). Although maximum values are located within the Vaca Muerta Formation (0,32 %), no clear trend for the entire system is recognized. Nevertheless, an important increase on the P content (> 0,17 %) is recorded within the transition interval (Fig. 12).

Sulfide group: The sulfide group is composed of Fe, Cu, Zn, S which is associated to sulfide authigenesis, strongly dependent on paleoredox conditions (Algeo and Maynard 2004, Tribovillard et al. 2006, Calvert and Pedersen 2007). Fe varies between 1 and 5 %, showing relatively high values within the first 200 m of the Vaca Muerta Formation. Upwards, a general decreasing trend until B4 (Fig. 12). Then a general increasing tendency is recorded, with a noticeable increase in the transition interval and a progressive increase for the rest of the column, reaching maximum values at the top of the Quintuco Formation (Fig. 12). Cu and S show a similar behavior. Their higher values are recorded in Vaca Muerta Formation, especially within the first 200 m. Then, they present a subtle decreasing tendency towards the top of Vaca Muerta Formation (Fig. 12). The transition interval is characterized by a depletion in both elements, Cu and S contents are low upwards, despite a local increase above the transition interval (Fig. 12). Zn values are extremely variable (15-1551 ppm), exhibiting the maximum values within the lower 220 m of the Vaca Muerta Formation, with an important depletion on the transition interval and a subtle increase on the upper 200 m of the Cerro La Visera Member (Fig. 12). Fe/S ratio remains invariable throughout the Vaca Muerta Formation, with a noticeable increase on the transition interval, and a general increasing trend from the base to the top of the Cerro La Visera Member (Fig. 12).

DISCUSSION AND INTEGRATED ANALYSIS

Mineralogy and diagenesis of the Vaca Muerta-Quintuco system

In the study area, the Vaca Muerta-Quintuco system underlies the Mulichinco and Agrio Formations (upper Mendoza Group), and the Bajada del Agrio and Neuquén Groups (Leanza and Hugo 1977, Rojas Vera *et al.* 2015). Consequently, it underwent considerable overburden which is reflected in the overmatured organic matter, which bear a Tmax about 520°C under Rock-Eval pyrolysis (Kietzmann *et al.* 2016a). Accordingly, a high-diagenetic mineralogical association mainly

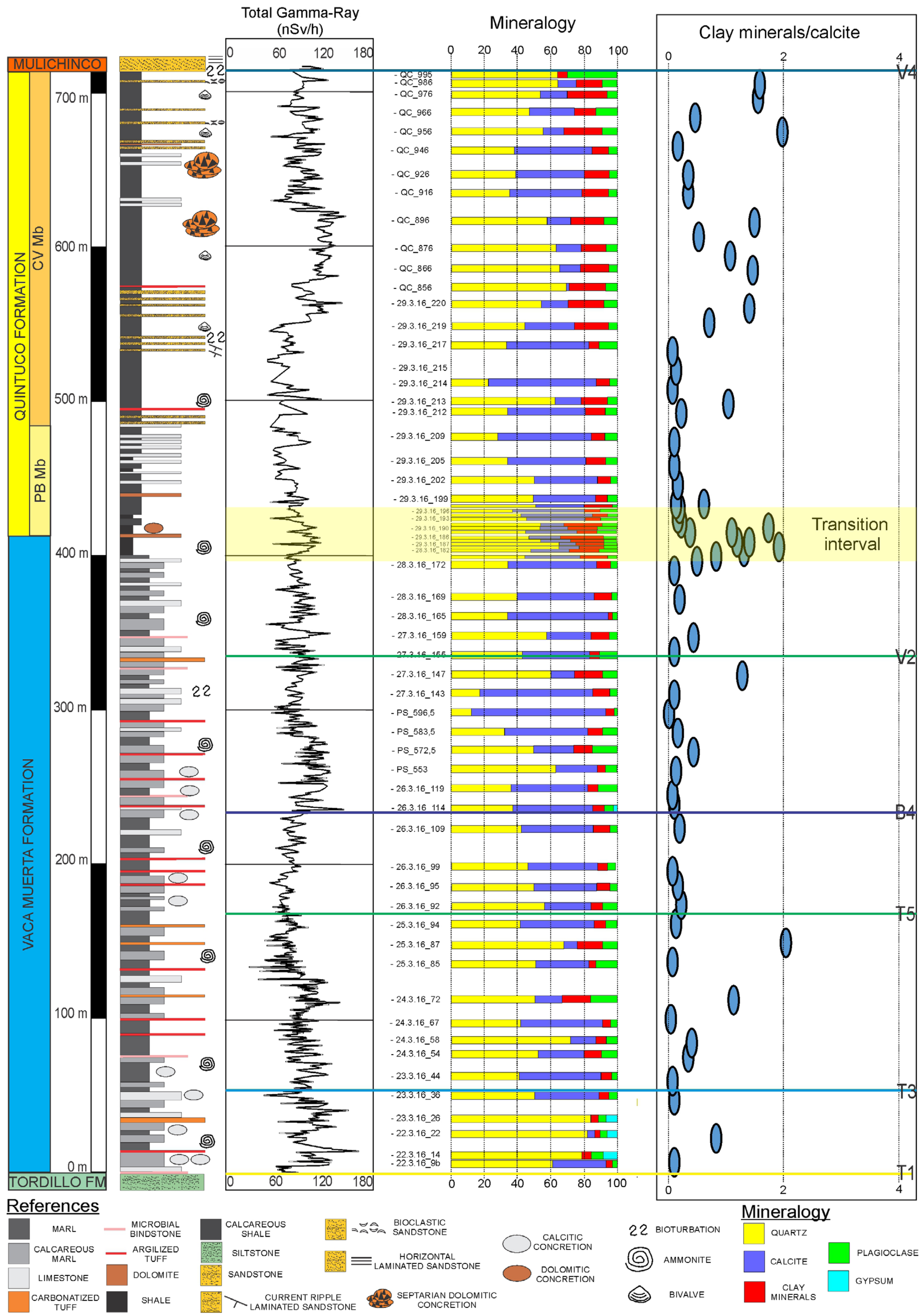

Figure 6. Schematic litholog of the Vaca Muerta-Quintuco system in the Puerta Curaco section. Mineral abundance in the bulk rock was calculated for quartz, calcite, clay minerals, plagioclase and gypsum. Clay mineral/calcite ratio is not represented in samples lacking calcite (22.3.16_14; 22.3.16_26; QC_995). T1, T3, T5, B4, V2, V4: regional stratigraphic surfaces from Desjardins *et al.* (2016).

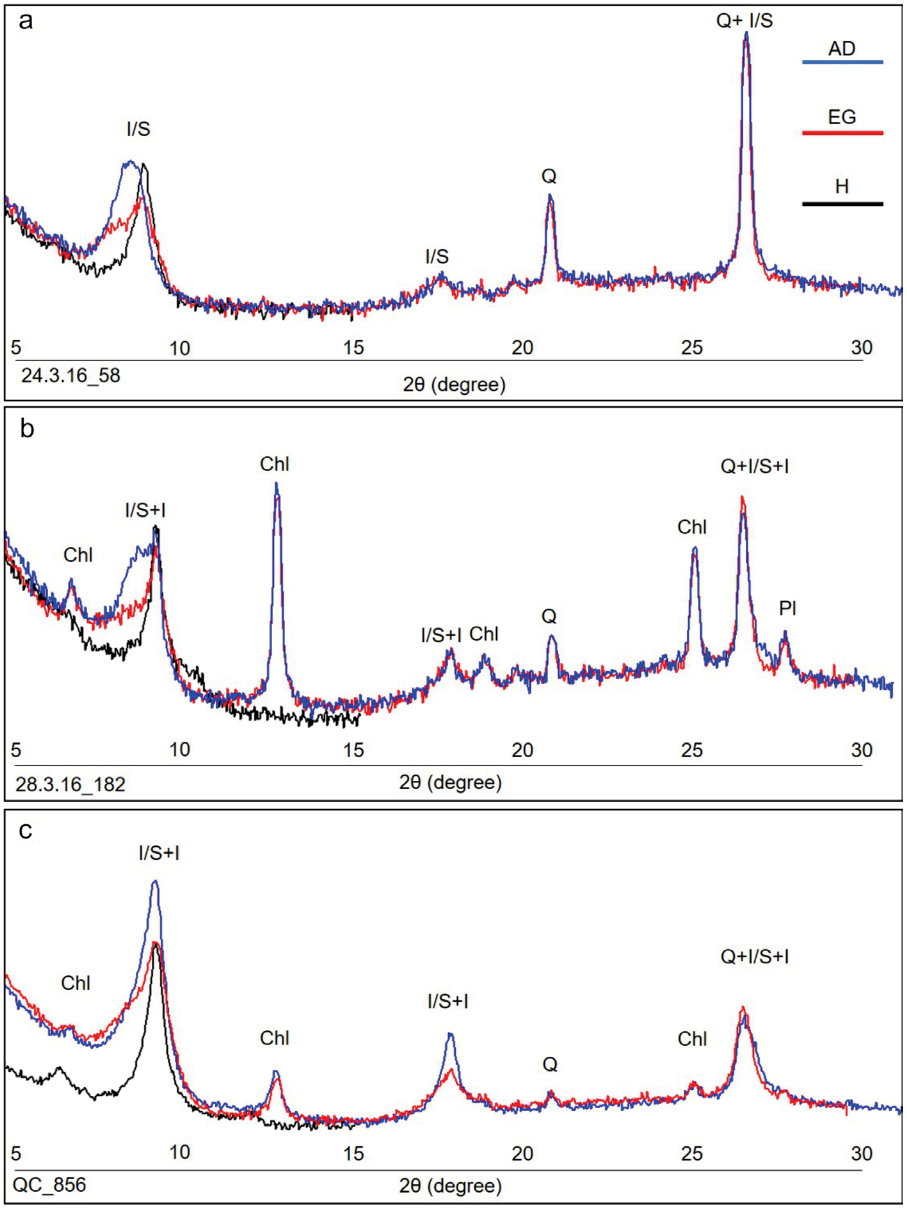

Figure 7. XRD patterns for the clay fraction below 2 µm. a) Marlstone of the Vaca Muerta Fm. dominated by high-ordered (R3) I/S. b) Calcareous mudstones of the PBMb (transition interval), dominated by chlorite and I/S+I. c) Mudstone of the CVMb, characterized by the presence of illitic material with some expandable phase and chlorite. AD: air-dried, EG: ethylene-glycol solvated, H: heated.

composed of quartz, plagioclase, calcite, high-ordered I/S and chlorite was found in the system (Capelli *et al.* 2017a).

Plagioclase was found throughout the entire column (Fig. 6). The XRD pattern preliminary suggests a Na-rich plagioclase, probably albite. Albite is a consequence of the complete transformation of Na-rich zeolites or the alteration of K-feldspar (*e.g.*, Coombs 1954, Land and Milliken, 1981). Since no significant K-feldspar is found throughout the system, K content is mainly assigned to the illitic minerals (*e.g.*, Adams and Weaver 1958, Cowan and Myers 1988).

The high-ordered I/S is a consequence of the progressive illitization process suffered by smectite layers (*e.g.*, Hower *et al.* 1976). The progressive transformation of smectite to illite via mixed-layer releases SiO_2 and Fe, favoring the precipitation of overgrowths on quartz and Fe-rich chlorite (*e.g.*, Hower *et al.* 1976, Boles and Franks 1979, Lee *et al.* 1985). Recently, Wilson *et al.* (2016) proposed that high-ordered I/S from shale reservoirs may precipitate under specific conditions from pore waters. This origin in the Vaca Muerta-Quintuco system should not be fully discarded.

Diagenesis may also modify Sr/Ca ratio (*e.g.*, Stoll and Schrag 2001). Primary biogenic calcites present a much higher Sr content than the secondary equilibrium abiogenic calcite. Therefore, diagenetic recrystallization (occurred during early diagenesis) results in loss of Sr to porewaters (Stoll and Schrag 2001). This may lead to the diagenetic precipitation of calcite with low Sr/Ca ratio. Increasing diagenesis may have produced a downward decreasing trend of the Sr/Ca ratio in the column (Fig. 11). Isolated maxima on the Sr/Ca ratio would represent primary variations in the bioclastic content.

Detrital input and organic productivity: implications on lithostratigraphy

The petrographic, geochemical, mineralogical and lithological variations recorded throughout the Vaca Muerta-Quintuco system suggest that sedimentation was controlled by a combination of processes: carbonate production, detrital contribution, mineral authigenesis and organic production within the water mass. The analysis allowed to discriminate 5 intervals (I1-I5) for the Vaca Muerta-Quintuco system in the Puerta Curaco section (Fig. 13).

-I1: The lower 170 m (CS 1 and CS 2) are characterized by relatively stable, low values of K, Th, Zr and Ti, suggesting a low contribution of detrital sedimentation to the outer carbonate ramp. The low correlation of Si-Zr and the low amounts of detrital quartz observed for the Vaca Muerta Formation marlstones, suggest that quartz detrital contribution is negligible (*e.g.*, Blood *et al.* 2013, Dowey and Taylor 2017). Quartz content can be associated to a biogenic source, probably linked to the abundance of radiolaria, combined with other factors such as the progressive illitization of smectite layers that yields silica for the formation of microcrystalline quartz (Fig. 7a) (*e.g.*, Hower *et al.* 1976). The important variations in calcite content are explained by the existence of high-frequency sequences, in which HSTs are enriched in calcite when compared to the TSTs (Kietzmann *et al.* 2016a).

U, V, Ni are insoluble under reducing conditions. So, these elements are usually richer in oxygen-depleted environments (*e.g.*, Tribovillard *et al.* 2006). Maximum

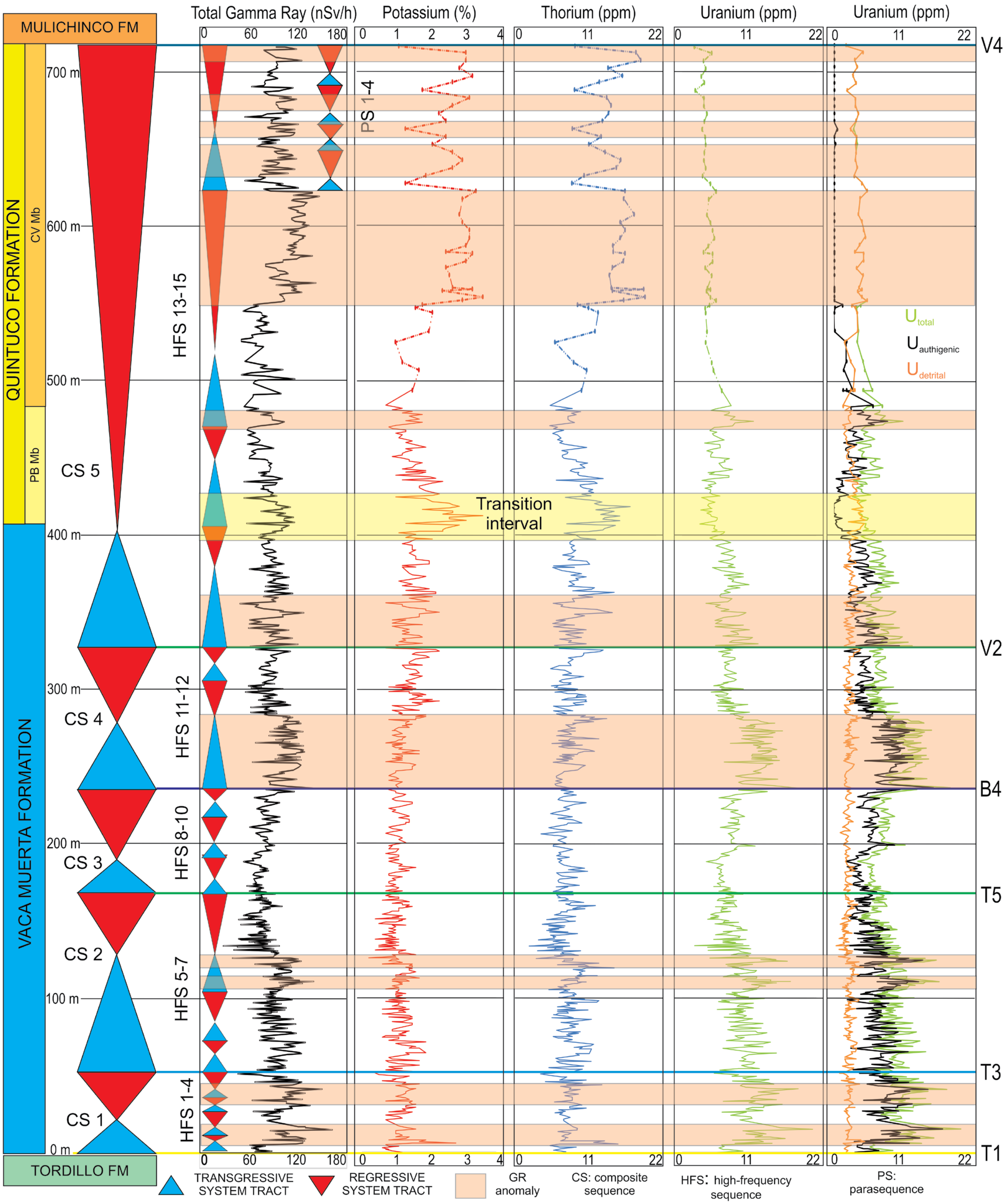

Figure 8. Spectral Gamma Ray log together with the lithostratigraphic and sequence stratigraphic subdivision for the Vaca Muerta-Quintuco system.

values of U, V and Ni are observed within the I1 interval (Figs. 12, 13), indicating high organic productivity in accordance to the TOC vertical trend (Kietzmann *et al.* 2016a, Eberli *et al.* 2017). This tendency presents a good correlation with Mo content, which is as a good proxy for redox conditions (see Tribovillard *et al.* 2006). The excellent correlation of Total GR and U (Fig. 9a) indicates that, for Vaca Muerta Formation (I1 and I2) the GR signal essentially responds to the organic content.

The (V/V+Ni) curve indicates that I1 was sedimented in an anoxic to intermittently euxinic environment (Fig. 12) (Hatch and Leventhal 1992), consistently with the lack of significant bioturbation observed in the Vaca Muerta Formation. Euxinic conditions were reached on the Tithonian transgression, leading to the formation of organic-rich levels found in the base of the Vaca Muerta Formation. An euxinic environment was proposed for that unit in the Picún Leufú depocenter (southern Neuquén Basin) (Legarreta and Villar 2015). Recent studies, also proposed an euxinic environment for the very basal deposits of the Vaca Muerta Formation in this depocenter, whereas the rest of the column was deposited under oxic/anoxic or fully oxygenated marine waters (Krim *et al.* 2017). In I1, euxinic conditions were reached on TST of CS-1 and on TST of HFS-7, suggesting limited water circulation through the basin. Within this interval, Zn and Cu present the higher values, associated to high organic matter content. Those metals, under anoxic conditions and during the sulfate reduction stage, are released from organic matter to pore waters, being usually present as solid solutions of pyrite crystals (Morse and Luther 1999, Tribovillard *et al.* 2006).

-I2: Within this interval, a general increase of clastic material is observed, which is indicated by the progressive increase of K (Figs. 8, 11). On the other hand, a decreasing trend of the organic-rich proxies is observed. An exception to this trend is recorded on the TST of the CS 4 (B4), where a 50 m thick interval with high U content is recorded. This level corresponds to an important regional transgressive event extensively represented on the basin (*e.g.*, Desjardins *et al.* 2016), also called "upper enriched zone" (*e.g.*, Marchal *et al.* 2016). This event led to high organic productivity, reflected in the high content of the elements of the organic group.

The Fe/S ratio remains almost invariable, indicating that both elements are strongly correlated to the authigenic pyrite content. The V/V+Ni ratio indicates predominantly anoxic to dysoxic conditions (Fig. 11), although euxinic conditions were reached on the TSTs of both CS-4 and CS-5. P, usually associated to high-productivity stages, may be not directly related to the supply of organic matter (*e.g.* Tribovillard *et al.* 2006). Indeed, within the Vaca Muerta Formation, there is not a vertical correlation between P and Mo (Fig. 12).

-I3: this interval is coincident with the transition interval and it is characterized by a sudden increment of Zr, Ti, Al and K, and a decrease of organic proxies and carbonate content, as shown in figure 11. These elements represent an important contribution of detrital material (Calvert and Pedersen 2007) mainly associated to an increase of clay minerals (Fig. 6). The correlation of Si-Zr (Fig. 10) suggests a detrital origin for quartz. Also, the significant increase on the Fe/S ratio reflects the increase of illite and chlorite contents, both with important amount of Fe as evidenced by their asymmetric XRD traces. Nevertheless, Fe may also be present in amorphous Fe-oxides not determined by XRD.

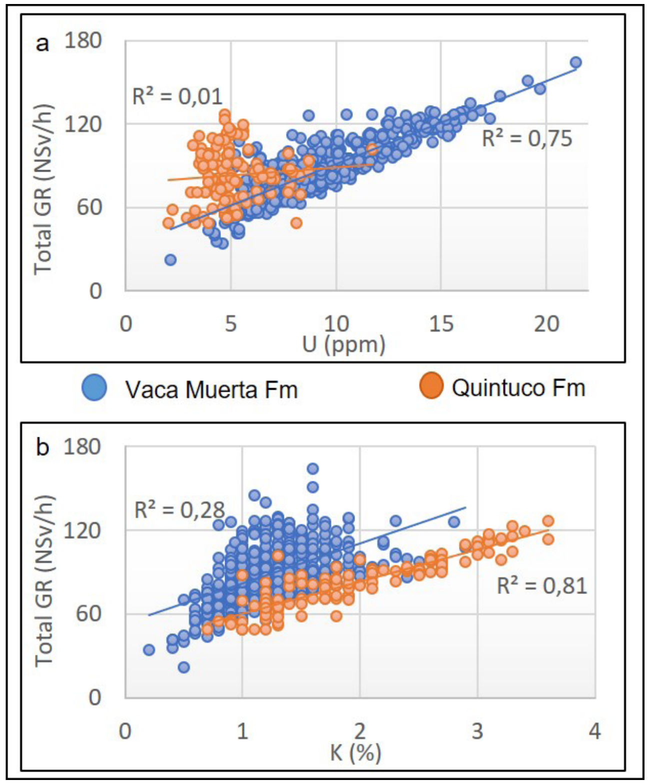

Figure 9. a) Cross-plot of Total GR vs U (ppm). They show good, positive correlation for the Vaca Muerta Formation (R^2: 0,75) and no correlation for the Quintuco Formation (R^2: 0,01). b) Cross-plot of Total GR vs K (%) showing no correlation for the Vaca Muerta Formation (R2: 0,28) and good, positive correlation for the Quintuco Formation (R^2: 0,81).

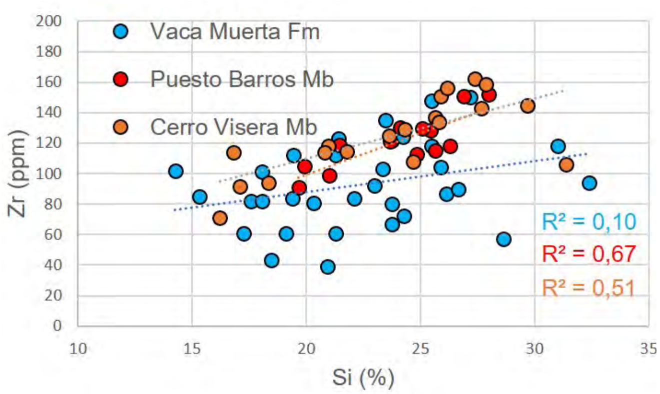

Figure 10. Zr vs Si cross-plot, showing different correlation in Vaca Muerta and Quintuco Formations.

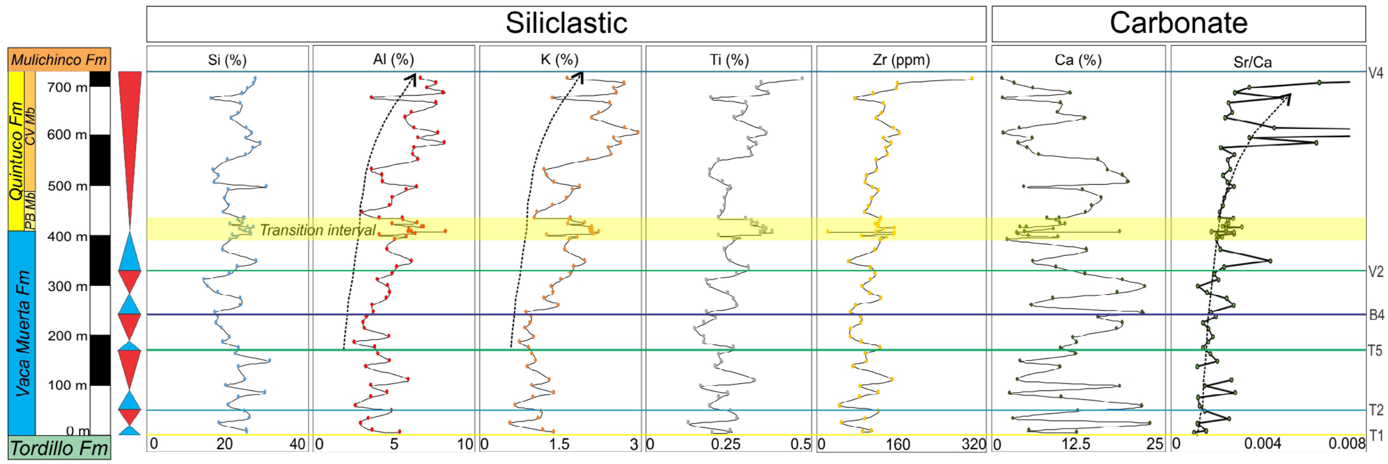

Figure 11. Major and trace elements of marlstones and mudstones associated to the siliciclastic and carbonate groups. Note the transition interval enriched in Al, K and Ti and Sr/Ca, and relative impoverished in Ca.

The high contribution of clastic material may be the consequence of an important base level fall, as observed on the seismic lines for this interval (see Sattler *et al.* 2016). The subtle increment of the Sr/Ca ratio reflects an important contribution of biogenic carbonate in the carbonate particles of the calcareous mudstones (*e.g.* Stoll and Schrag 2001). The increase on the Sr/Ca ratio suggests that the carbonate of the matrix presents a richer bioclastic contribution. The I3 is characterized by relative high and stable values of P, indicating an enrichment in P during the transition from Vaca Muerta to Quintuco Formations (Fig. 12), also evidenced by the presence of fluorapatite. The enrichment of P in this transition interval may also be linked to a sea-level fall, where reworking and concentration of phosphatic particles may occur (*e.g.*, Föllmi 1996 and references therein). For example, in the Cerro Salado area (southern of Puerta Curaco), important accumulation of phosphatic particles (P_2O_5 <8 %) has been recorded in regressive system tracts of the Quintuco Formation (Medina *et al.* 2016).

-I4: this interval spans the upper part of the Puesto Barros Member and the basal meters of the Cerro La Visera Member (Fig. 13). It is characterized by a relative decrease of detrital proxies, (Fig. 11) and a subtle increase of organic proxies when compared to I3. Within this interval, a subtle increment of U, Mo, S and Zn is recorded, mainly developed on the TST of the HFS-15 (Figs. 8, 12). A parallel increase of Ca and carbonate suggest the restoration of the carbonate ramp environment. I4 is then similar to I2, but with less contribution or organic matter, as suggested by the content of the organic-related elements.

-I5: this interval comprises the rest of Cerro La Visera Member (Fig. 13) and represents the final establishment of the mixed siliclastic-carbonate shelf of the Quintuco Formation (Kietzmann *et al.* 2016a). It is characterized by an important increase of K, Th, Al, Ti and Zr, concurrent with the appearance of siltstones and occasional, fine-grained, rippled sandstones, as well as the abundant bivalve fragments and sponge spicules. V/(V+Ni) ratio indicates that, although the water conditions were still anoxic, fluctuations to more dysoxic or even oxic environments were recorded (Fig. 12). The high Sr/Ca ratios in this interval reflect the important contribution of bioclastic carbonate, a consequence of the shallowing upwards environment. The Sr content of seawater was probably increased by the release of pore waters enriched in Sr due to the recrystallization of shelf aragonite to calcite on inner exposed platforms (*e.g.* Schlanger 1988, Stoll and Schrag 2001).

Paleoenvironmental changes inferred through geochemical and mineralogical variations

The Vaca Muerta Formation is characterized by relative low values of detrital proxies (Figs. 11,13). On the other hand, the high content of sulfide-associated metals (Zn, Cu) and the organic-proxies indicates abundance of organic matter. A progressive input of detrital material is evidenced in I2, (Figs. 8, 13), generating a relative reduction of organic matter content, as suggested by the decrease of organic-proxies. An anoxic environment prevailed during Vaca Muerta Formation sedimentation, although euxinic conditions were occasionally reached, especially in I1 (Fig. 12). Organic matter accumulation is concentrated within TSTs of both, CS and HFS for the Vaca Muerta Formation outer ramp deposits, which were submitted to relative low sedimentation rates (25 cm/1000 years, Kietzmann *et al.* 2016). Furthermore, high sea-level and lower sedimentation rates generated oxygen-depleted conditions that allowed the accumulation of organic matter with insignificant terrigenous dilution.

The carbonate ramp environment (Vaca Muerta Formation) was suddenly submitted to a significant contribution of detrital material, especially illite, chlorite and also detrital quartz. The contribution of detrital material was a consequence of a relative sea-level fall and it is characteristic of the the transition interval (I3), representing the first evidence in Puerta Curaco area of the establishment of the mixed siliciclastic-carbonate shelf, typical of the Quintuco Formation. V/V(+Ni) ratio does not suggest significant paleoredox changes for the transition interval and for the rest of the Quintuco Formation, where anoxic conditions still prevailed. Consequently, the lower content of organic matter was caused by the increased clastic input and not by

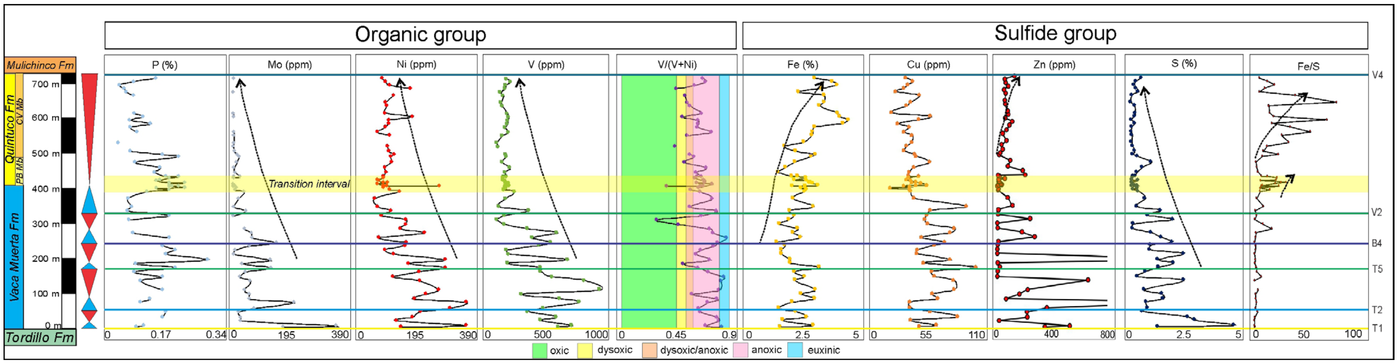

Figure 12. Major and trace elements of organic and sulfide groups. The transition interval is characterized by an increase on P, Fe, Cu and Fe/S, with a notable decrease of V, N, Mo and S.

significant changes in the oxygenation of the environment. This is in agreement with the higher sedimentation rate for the Quintuco Formation, calculated in 100-120 cm/1000 years (Kietzmann *et al.* 2016a).

CONCLUSIONS

The Vaca Muerta Formation in the Puerta Curaco section presents a thickness of 407 m. It is characterized by a succession of black, laminated marlstones and limestones, with commonly interbedded tuffs and beef veins. Overlaying the Vaca Muerta Formation, the Quintuco Formation presents a thickness of 309 m and consists on calcareous mudstones, siltstones, limestones, dolostones and fine-grained sandstones.

The Quintuco Formation is subdivided into two members: the lower Puesto Barros Member (76 m), composed by black calcareous mudstones, dolomite concretions and limestones, and the upper Cerro La Visera Member (233 m), characterized by calcareous mudstones, dolomite concretions and interbedded siltstones and fine-grained sandstones.

The boundary between the Vaca Muerta and Quintuco Formations is set at the lower dolostone bed (407 m from the base of the Vaca Muerta Formation). The dolostone bed is easily recognizable in the outcrops and can be extrapolated to the subsurface in neighboring blocks.

Natural radioactivity of the Vaca Muerta Formation is strongly dependent on the U content, while K and Th contributions are less important. The opposite is true within the Quintuco Formation, where total GR is strongly influenced by the K and Th content, and U contribution is almost negligible.

Mineralogical, geochemical and sedimentological features allow us to discriminate 5 intervals in the Vaca Muerta - Quintuco system. The I1 and I2 are developed within the Vaca Muerta Formation, characterized by carbonate sedimentation, essentially deposited under anoxic conditions, with intermittent euxinic periods. I1 is enriched in organic-matter, with insignificant contribution of detrital material and quartz of non-detrital origin. The anomalous values of U are associated to organic-rich intervals, developed within TSTs, that may have resulted from euxinic conditions. I2 is also enriched in organic material, although a progressive increment on detrital contribution is evidenced.

I3 is developed within the transition interval between Vaca Muerta and Quintuco Formations and is characterized by a noticeable increment on K and Th, an increase in the clay minerals/calcite ratio, as well as an increase on other detrital proxies like Al, K and Ti, combined with detrital quartz and a general decrease on the organic-related elements. The high abundance of detrital material is interpreted as a consequence of a sea level fall. I4 is coincident with the Puesto Barros Member in Quintuco Formation and presents a lithology similar to Vaca Muerta Formation (I2), suggesting that the carbonate ramp sedimentation was partially restored. Finally, I5, is developed in the Cerro La Visera Member, below the Intravalanginian unconformity, being characterized by an important contribution of detrital quartz and clay minerals. In spite of the progressive increase on the detrital material, geochemical proxies suggest that the anoxic environment still prevailed during the accumulation of the Quintuco Formation.

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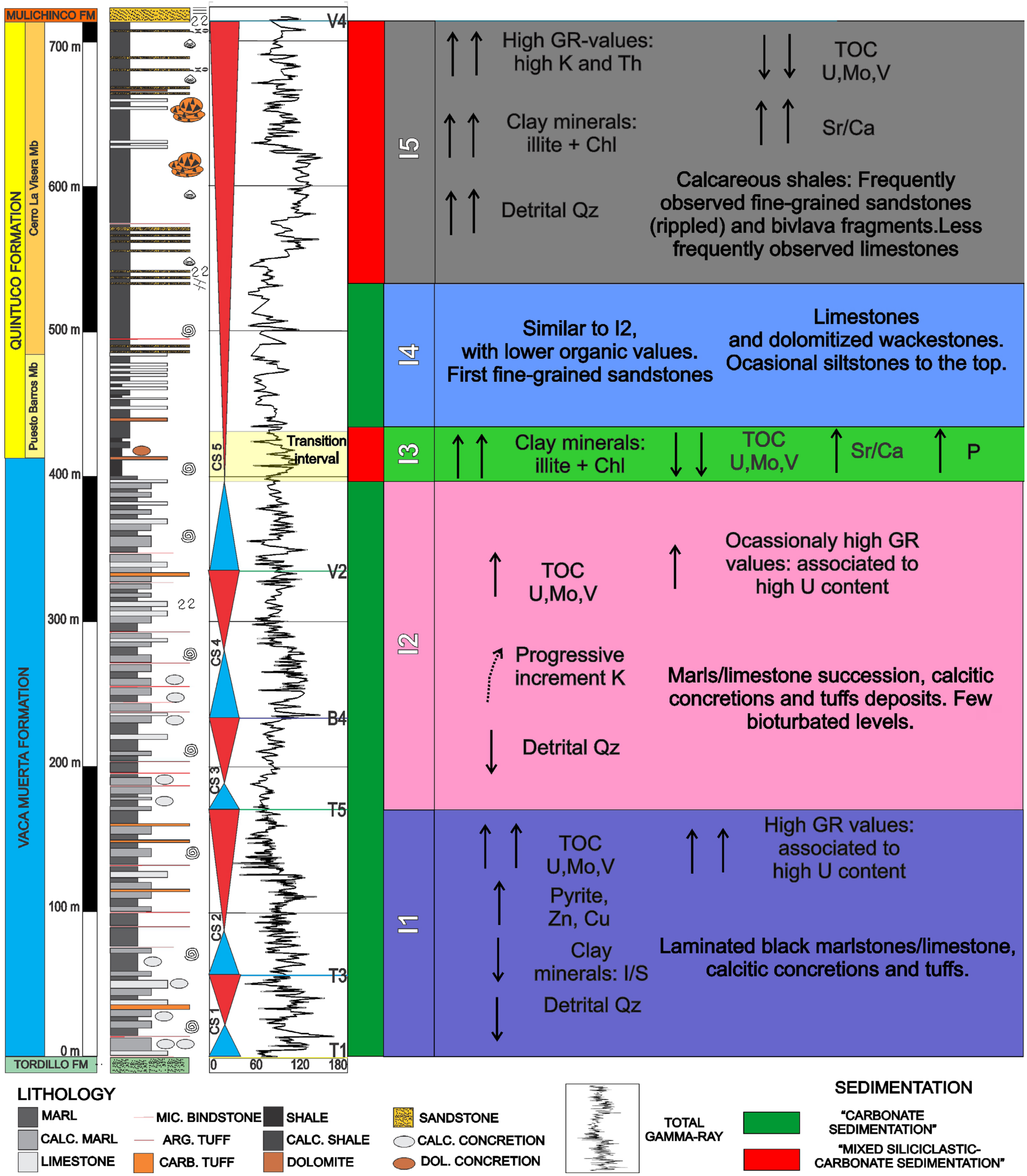

Figure 13. Schematic litholog of the Vaca Muerta-Quintuco system in Puerta Curaco area, exhibiting the main geochemical/sedimentological intervals (I1-5).

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