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# ORGANIC GEOCHEMISTRY AND CHEMOSTRATIGRAPHY OF THE LOS MOLLES FORMATION, NEUQUÉN BASIN, ARGENTINA

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## Abstract

The present study comprises the sampling carried out in an outcrop of the Los Molles Formation at the Puente Picún Leufú area, Neuquén Province, Argentina. A section of 22.6 m thickness ("M3") was described and 22 samples were analysed at the Y-TEC laboratories. The main objective was the characterization of the organic petrology and organic geochemistry in terms of different parameters of quantity, quality and maturity of the organic matter to evaluate the potential of hydrocarbon generation along with chemostratigraphy analyses.The study included the determination of Total Organic Carbon content (TOC) by pyrolysis using a ROCK EVAL 6 equipment, and organic petrology by means of an Axio-Imager microscope with a CRAIC coupled spectrometer and XRF fluorometry. Major, minor and trace elements were characterized by X ray fluorescence. The results obtained showed TOC values between 0.69 and 1.84% wt., and a distribution of HI values in the sequence between 5 - 313 mg HC / g TOC. The organic petrology shows that the content of kerogen was strongly continental, dominated mainly by superior plant material, miospores, resins of vegetal origin, fluorescent and non-fluorescent amorphous organic matter with a low contribution of type II kerogen. The values of Tmax obtained from the pyrolysis are between 423 – 447 °C immature and early oil window in concordance with vitrinite reflectance values (0.38% - 0.45%). Paleoredox elements such as V, As, Zn, Mo, and S, were consistent with the reducing setting related to high TOC values and to kerogen quality, proving the occurrence of anoxic and euxinic environments. From the organic geochemical perspective, the Los Molles Formation in this sector of the Neuquén Basin is a regular to good source rock, with predominant type III kerogen, and in a low proportion type II, in an immature state with potential to generate hydrocarbons, mainly gas.

**Keywords:** organic petrology, organic matter, generation potential

## Introduction

The objective of this research was to estimate quantity, quality and maturity of the organic matter (OM) and the hydrocarbon generation potential of the Los Molles Formation by different techniques. The studies were carried out on the stratigraphic section near "Puente Picún Leufú" area, Neuquén Province, Argentina. They consist of organic petrology, organic geochemistry, chemostratigraphy by XRF and the interpretation of the relations found in the different parameters obtained. The Neuquén Basin is a retroarc basin located in the central-western sector of Argentina, originated during the Late Triassic from a series of rift-type depocenters, which constituted an important sedimentation with thicknesses close to 7,000 meters, from marine to continental deposits during the Jurassic. Cuyo Group (Lower to Middle Jurassic) represents the first episode of marine sedimentation after the configuration of the basin. According to the traditional stratigraphic scheme, the deposits starts with black shales from the interior of the basin to the external platform, known as the Los Molles Formation (Weaver, 1931), which pass to the siliciclastic sequence assigned to the Lajas Formation (Herrero Ducloux, 1946). The Los Molles Formation is recognized as one of the sourcerock in the Neuquén Basin (Uliana, *et al.,* 1999 and Brisson, 2015). Brisson (2015) describes the Los Molles Formation as a generally modest quality rock, with less than 2% of TOC (Total Organic Carbon), that represents a marine environment with contribution of continental material, that confers characteristics of a mixture of type II/III kerogens. Quattrocchio *et al.* (1996), García (1998), Martínez (1999), Martínez *et al.* (2001) and García *et al.* (1994, 2000) made contributions associated to the palynostratigraphy and palynofacies of the Cuyo Group. More recently, Martínez (Martinez *et al.,* 2008) related the palynofacies of the Los Molles Formation with organic geochemistry data, characterizing depositional paleoenvironments and oleogenetic potential of sediments. Recently, valuable contributions have been made regarding the occurrence of heavy metals present in sediments with organic content using techniques such as X-ray fluorescence (McColloch 2016), which were

applied to rock samples of the D-129 Fm., Golfo San Jorge Basin (Larriestra *et al.,* 2015).

## Methods

The field work included the stratigraphic survey and systematic sampling of the named as “M3“profile in the locality of Puente Picún Leufú, Neuquén Province, Argentina (S39°12' 20.9''- W 70° 0.4' 22.8'' ). The samples were taken in equidistant segments of approximately 1-1.5 m. The sampled rocks correspond to grey siltstones that forming tabular layers, with flat base and top, fine lamination, with variable clay proportion. 22 samples were taken and processed at the Y-TEC laboratories, to perform petrology and organic geochemistry studies regarding different parameters such as quantity, quality and maturity of organic matter. The analyses carried out included the determination of TOC, S1, S2, S3, Tmax, HI, IO, IP and other parameters through pyrolysis using ROCK EVAL 6 analyser for all samples. In representative profile levels some samples were studied by organic petrology, using Zeiss Axio-Imager A2m microscope to identify palynofacies, and in 5 samples, reflected light for macerals identification and vitrinite reflectance (figure 2a), with Zeiss Axio-microscope Imager A2m with a CRAIC PV 508 spectrometer and CoalPro software. For the analysis of major, minor and trace elements (vanadium, molybdenum, potassium, rubidium, arsenic, zinc, sulphur) all the samples were ground at 250 µm fraction and a Thermo Niton Gold XL3T portable X-ray fluorometer was used.

## Results and Discussion

The sedimentary sequence is characterized by a dominance of thin laminae grey siltstones interbedded with claystones levels, scarce pyroclastic deposits in the middle of the sequence and a sandstone level at the top. The presence of mollusc shells, ammonites, belemnites and plant debris were found mainly at the first half of the sequence. The organic geochemistry analysis yielded good organic content in three segments of the sequence, all showing TOC values between 1– 2%. The basal segment was characterized by having TOC values of 1.6 - 1.8%, type II/III kerogen with a maximum HI of 303 mg HC/g TOC, and S2 values of 5,61 mg HC/g. The evidence indicates that it was clearly an euxinic environment, due to the high values of V and Mo (ppm) registered (Trivobillard *et al.,* 2006). Kerogen showed an amorphous / terrigenous proportion of 50% for each type. The middle sector, with values of TOC of 1.8%, registered high concentrations of V but the absence of Mo, resulting in an anoxic deposition environment (figure 1). The organic matter type obtained by pyrolysis in this sector corresponds with a type III kerogen. The top of the sequence showed values of TOC of 1.8% corresponding to a type III kerogen verified by the pseudo Van Krevelen diagram and visualized in transmitted light (figure 2b). The K/Rb ratio curve displayed an increasing trend towards the top of the sequence, opposed to the HI curve, indicating the K content of the plant debris (K is a macronutrient of vascular plants while Rb is not). The S curve showed a strong correlation with the type III kerogen in the middle and the upper section. As and Zn curves showed a typical increment related to reducing environments. The concentration of Ca correlated very well with MinC values (mineral Carbon) assuming variable concentrations of $CaCO_3$ (figure 1). Tmax values obtained ranged from 423 to 447 °C; and in reflected light, the vitrinite reflectance results were 0.38% - 0.45%. Both values indicate an immature state of the source rock.

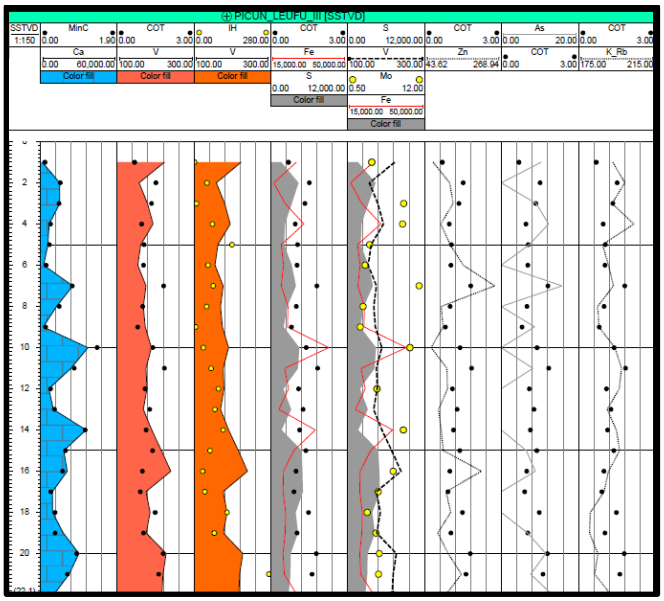

**Figure 1.** Integrated organic and inorganic geochemical profiles. From left to right: calcium and mineral carbon ($CaCO_3$); TOC and vanadium; HI and vanadium; TOC, iron and sulphur; sulphur, vanadium, molybdenum and iron; TOC and zinc; TOC and arsenic; TOC and potassium / rubidium.

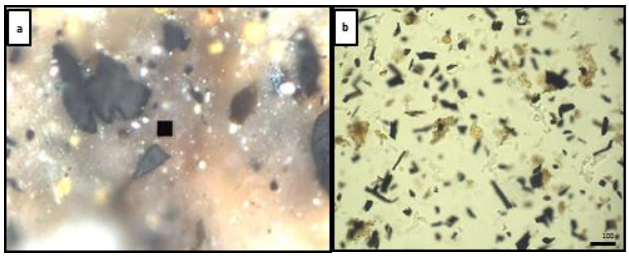

**Figure 2a)** Organic matter in reflected light. The black dot indicates the size of the measurement area (5x5 microns). **2b)** Kerogen in transmitted light. Palynofacies corresponding to type III kerogen characterized by the presence of abundant opaque phytoclasts and, subordinate miospores.

## Conclusions

The organic geochemistry of the Los Molles Formation in this sector of the basin can be considered a regular to good source rock, with predominant type III kerogen and in a minor proportion type III/II, in immature state with the potential to generate hydrocarbons, mainly gas. Throughout the sequence, most of the organic matter deposition took place under euxinic conditions. As seen very clearly at the base of the sequence, the algal inputs were always related to high Mo and V concentrations, while terrigenous material wasn't always related to those trace elements. The K/Rb ratio curve correlated well with the presence of terrigenous material, probably related to the content of this macronutrient being carried within the phytoclasts, and inversely related to the HI. This situation may be the result of the quieter anoxic / euxinic conditions required for the accumulation of planktonic OM in the face of suboxic conditions sufficient for the deposition of terrigenous organic remains. Type III/II kerogen was deposited mainly under euxinic conditions, while type III kerogen is more terrigenous and correlated well with the K/Rb ratio curve (anoxic condition). The S curve showed a strong correlation with type III kerogen in the middle and upper section, suggesting a sulphidic environment for plant debris accumulation. This set of observations suggests the possibility of having inorganic elements (proxies) potentially able to estimate the total organic carbon concentration, as well as the type of kerogen present, without the need to destroy the sample by acid attack or by pyrolysis, in addition to have a more detailed sampling capacity. Organic geochemistry, organic petrology and chemostratigraphy are tools that, when integrated, could substantially reduce the uncertainty associated with the analysis of source rocks.

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