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Porosity development and the influence of pore size on the CH_4 adsorption capacity of a shale oil reservoir (Upper Cretaceous) from Colombia. Role of solid bitumen

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ABSTRACT

The La Luna Formation of Turonian–Santonian age has recently been described as a reservoir of shale oil type which is located in the Middle Magdalena Valley Basin (MMV) of Colombia. Two of the members of this formation, Galembo (GM at the top) and Salada (SM at the bottom) have previously been investigated by Juliao et al. (2015) to determine their organic composition, maturity and hydrocarbon potential as well as their macro- and mesoporosity characteristics by means of mercury intrusion porosimetry (MIP analysis). The present work, which is a continuation of the previous one, focuses on the study of the porosity using low pressure N_2 and CO_2 adsorption analysis of both members in the determination of CH_4 adsorption capacity and in the establishment of the corresponding relationships with the pore size (micropore size). The role played by the solid bitumen (expressed as TOC content) of the lower sedimentary levels of both members (GM and SM) in the development of the porosity properties should be emphasized. The results obtained from this work demonstrate that: (i) the predominant types of organic populations (kerogen and solid bitumen) in the sedimentary levels of this shale oil reservoir, that show a narrow degree of maturity, are the main factors controlling porosity development and consequently CH_4 adsorption and storage capacity. (ii) The kerogen rich-levels (upper part of GM and SM) are mainly macro- and mesoporous corresponding this porosity to that of the primary organic matter and the inorganics and there is no relationship between this porosity and the variation in TOC content. (iii) The amount of porosity measured by N_2 adsorption in the kerogen-rich levels is influenced by the content of free hydrocarbons occluded in the pores (S1). (iv) Porosity (mainly microporosity) development in the lower levels of GM and SM seems to be linked to the presence/absence and the amount of solid bitumen, as demonstrated by the close relationship existing with the TOC content. Therefore, solid bitumen is the host of porosity. (v) The microporosity developed in the sedimentary levels with solid bitumen content strongly influences the CH_4 adsorption capacity although the relationship has been found to be complex as it is influenced by the micropore size and therefore, by the density of the CH_4. Finally, this study highlights the importance of organic petrography in detecting the solid bitumen, which is the organic component that explains all variation in the textural properties of GM and SM, and which eluded detection by all other techniques.

1. Introduction

The La Luna Formation (Turonian–Santonian, Upper Cretaceous) is considered to be one of the main hydrocarbon source rocks in the Middle Magdalena Valley Basin (MMV) in Colombia (Morales et al., 1958; Zumberge, 1984; Schamel, 1991; Montgomery, 1992; Rangel et al., 2000, Marquez et al., 2014) and an organic matter-rich reservoir of the shale oil type due to its significant resources of recoverable oil (*e.g.*, Pérez et al., 2013; Rojas et al., 2013; Juliao et al., 2013, 2015).

In a previous paper, Juliao et al. (2015) carried out a detailed petrographic, geochemical and porosity (Mercury Intrusion Porosimetry, MIP) research study on two of the members of this formation, the Galembo and Salada Members which are located at the upper and lower parts of the La Luna Formation, respectively. The La Luna Formation was sampled at the center part of the Magdalena Middle Valley Basin (MMV, Colombia). The results obtained in that work permitted an evaluation of the organic composition (kerogen type II, solid bitumen and hydrocarbons, unevenly distributed throughout the members of this formation), the degree of maturity (oil window stage), hydrocarbon potential and porosity properties of both members of the La Luna Formation. Moreover, it also revealed the different trends in porosity development and pore size distribution (as determined by MIP) in the

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sedimentary levels characterized by a predominance and/or high content of solid bitumen with respect to the levels in which kerogen type II was the predominant organic component. In fact, in these kerogen (type II) rich levels the pore size distribution was found to have developed in the range of mesopores and macropores of small size, whereas the solid bitumen-rich levels showed a predominance of pores of small pore size with a modal pore throat diameter of less than 10 nm. In light of these findings and the fact that the preliminary adsorption data obtained for all the studied samples had already indicated the development of some microporosity, particularly significant in the case of solid bitumen-rich levels, the objectives of the present work are:

- to quantify the meso- and microporosity, particularly that of smallest size in the La Luna (Galembo and Salada Members) shale oil reservoir, and to explain the different porosities developed by the various organic populations identified by Juliao et al. (2015),
- to establish the relationship between the volume of micropores, pore size and variation in CH_4 adsorption capacity of the various organic populations,
- to explain the relationships (or the lack of relationship) between porosity and TOC content as a function of the type of organic populations present in the La Luna Formation.

Thus, this article is a continuation of that of Juliao et al. (2015) and will provide critical data for understanding the influence of the various types of organic matter, particularly the presence of solid bitumen, on the development of porosity, pore structure and pore size, and also on CH_4 adsorption/retention in the La Luna Formation. The importance of solid bitumen in hydrocarbon reservoirs (tight gas siltstone reservoir) in relation to the rock porosity is an issue that has also been raised by Sanei et al. (2015). The study of the porosity and pore size distribution of shale gas and for extension in shale oil rocks is important as these textural parameters are one of the key parameters for evaluating the quality of this type of rocks, their capacity retaining hydrocarbons (oil and gas in place), and their potential for exploitation (Wang and Reed, 2009; Loucks et al., 2009, 2012; Milner et al., 2010; Schieber, 2010; Sondergeld et al., 2010; Curtis et al., 2011a,b, 2012; Tian et al. 2013; Reed et al., 2014; Al Hinai et al., 2014; Chen et al., 2015; Xiong et al., 2015 among other). Finally, this work demonstrates the capital importance of organic petrographic studies for interpreting some variations in geochemical parameters (such as TOC and Tmax) determined by analysis on the whole rock that at times provide a limited information.

2. Geological setting

The Middle Magdalena Valley (MMV) is an intermountain sedimentary basin, and an asymmetric tectonic depression, located between the Central and Oriental Ranges in Colombia (Mojica and Franco, 1990; Rolón, 2004). The basin is a back-arc rifting that underwent a slow subsidence rate towards the west and faster subsidence towards the east side resulting in a configuration typical of a half-graben basin. The borders of the basin are tectonic and made up of a set of complex folds and faults.

The MMV is filled with sediments from the Upper Triassic (which unconformably lies on the Precambrian continental basement) to Pleistocene grouped into 5 sedimentary sequences that are separated by major unconformities. Sedimentary sequence number 3 (originated in a post-rift phase) contains the Turonian and Conacian marine deposits represented by the La Luna Formation (Fig. 1). The La Luna Formation is made up of thin-bedded, laminated, dense, dark, gray-to-black colored limestone and calcareous shales, with abundant laminated and finely disseminated organic matter, and from the bottom to the top, it is subdivided into three members: Salada, Pujamana and Galembo

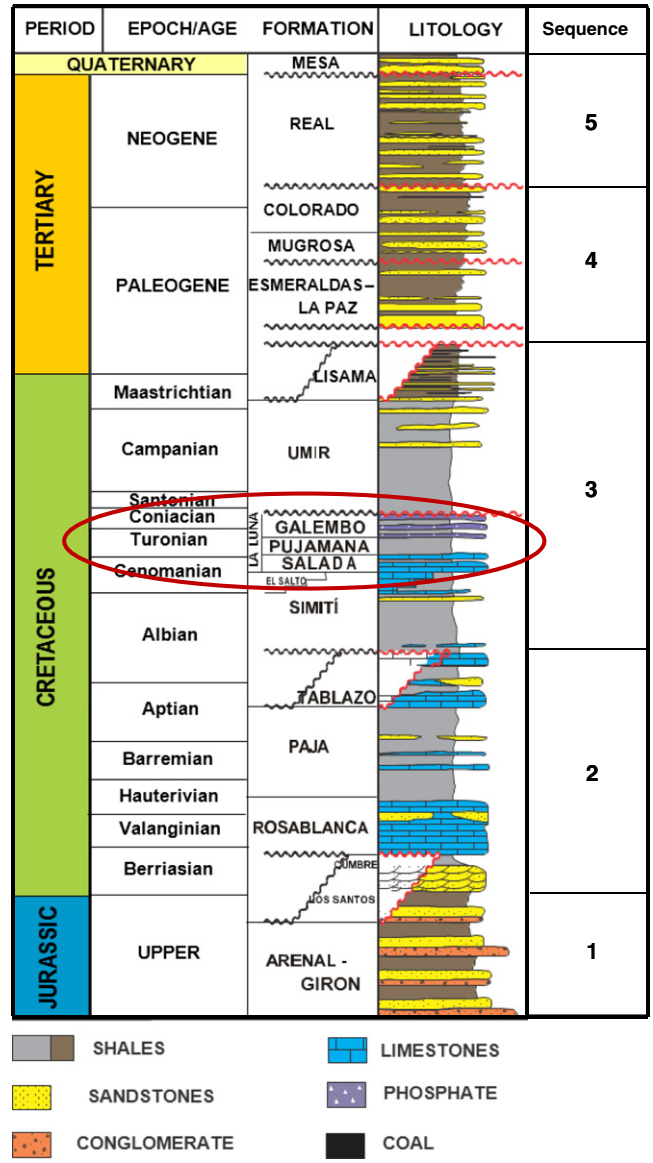

Fig. 1. Stratigraphic cross-section of the sedimentary sequences identified in the MMV basin and location of the La Luna Formation (modified from Rolón, 2004).

(Morales et al., 1958). This study focuses only on the organic-rich Galembo and Salada Members (considered as shale oil reservoirs) that were sampled from a core well perforated in the central part of the MMV basin such as it has been described in Juliao et al. (2015).

3. Analytical procedures

The samples studied in this work are the same as those used by Juliao et al. (2015). All the samples were prepared following the corresponding analytical procedures necessary for microscopic, textural and adsorption capacity study employing low-pressure N_2 and CO_2 adsorption-desorption isotherms, and CH_4 adsorption capacity analysis.

3.1. Microscopic characterization

Morphological analysis of some of the organic matter components found in the Galembo and Salada Members was carried out by means of optical microscopy using a DM 4500P Leica microscope fitted with a DFC 420C Leica camera and the corresponding software to capture and analyze the images. Samples were also examined using a Scanning Electron Microscope (FEI, Quanta FEG 650 model) equipped with an