PETROGRAPHIC AND PETROPHYSICAL CHARACTERIZATION OF THE EAGLE FORD 
SHALE IN LA SALLE AND GONZALES COUNTIES, GULF COAST REGION, TEXAS 

by

Sebastian Ramiro-Ramirez
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Geology).

Golden, Colorado

Date ______________

Signed: ____________________________
Sebastian Ramiro Ramirez

Signed: ____________________________
Dr. Stephen A. Sonnenberg
Thesis Advisor

Golden, Colorado

Date ______________

Signed: ____________________________
Dr. Paul Santi
Professor and Head
Department of Geology and Geological Engineering
ABSTRACT

The Eagle Ford Shale is an organic-rich marine carbonate-dominated mudrock located in the Gulf Coast Region, Texas. This mudrock was deposited during the Late Cretaceous and is composed of two main members: the lower and the upper Eagle Ford, which are associated to marine transgression and regression episodes respectively. Petrographic analysis of two cores from wells located in Gonzales (Well #1) and La Salle (Well #2) counties indicates that the Eagle Ford Shale has a strong cyclic character. Eight different facies and six microfacies were recognized at different well depths. A paleontologic study was carried out to better characterize the Eagle Ford Shale, where both benthonic and planktonic microfossils were identified. The most abundant microorganisms are foraminifera, although echinoderms, bivalves, fish bones, radiolaria, coccoliths and calcispheres are also present. This diversity in microfossils reinforces the cyclic character of the Eagle Ford. Contrary to the commonly believed idea that marine transgression implies deep marine anoxic conditions, this study indicates that it is not necessarily true. Instead, marine transgression may also lead to shallow marine conditions where benthonic organisms are abundant, similar to what is observed in the lower Eagle Ford at Well #2.

Pore system was characterized at both well locations by combining water immersion porosimetry (WIP), mercury injection capillary pressure (MICP) and scanning electron microscopy (SEM). Total porosity results indicated that WIP overstates the total porosity when clay content is above 50 wt. %. MICP shows more reliable total porosity values where mineralogy does not apparently affect the experiment final results. Total porosity ranges between 0.32-10.27 percent, where most pore throats diameters fall within the nanopore to micropore size range. Intraparticle pores within the organic matter are dominant in the Eagle Ford, especially in Well #2 where thermal maturity is higher compared to Well #1.
Hydrocarbon potential was studied by using both the Basic/Bulk-Rock and Institut Français du Pétrole Energies Nouvelles (IFPEN) Shale Play Rock-Eval pyrolysis methods. The IFPEN Shale Play method allows to a better quantification of the hydrocarbons in unconventional plays compared to the Basic/Bulk-Rock method. The average increase in hydrocarbons quantification using the new method is 25.69 percent. The intervals with higher hydrocarbon content are the lower Eagle Ford at Well #2 location (6.68-22.69 mg HC/g rock) and the lower portion of the upper Eagle Ford at Well #1 location (6.74-8.22 mg HC/g rock). Pyrolysis analysis was coupled with petrographic study on SEM. Detrital and secondary organic matters were recognized in both well locations, where secondary organic matter is dominant. A strong correlation between hydrocarbon potential and foraminifera test chamber cementation was found. Well intervals where foraminifera test chambers are filled with kaolinite and secondary organic matter present higher oil-in-place (OIP) compared to those intervals where the test chambers are cemented with calcite. Likewise, intraparticle organic matter porosity is denser at those intervals with higher potential in terms of OIP.
TABLE OF CONTENTS

ABSTRACT ............................................................................................................................................... iii

LIST OF FIGURES ................................................................................................................................ viii

LIST OF TABLES .................................................................................................................................. xiii

AKNOWLEDGEMENTS ...................................................................................................................... xiv

CHAPTER 1 INTRODUCTION ..................................................................................................... 1

1.1 Study area ........................................................................................................................... 2

1.2 Objective ............................................................................................................................. 2

1.3 Dataset and methodology ................................................................................................. 4

CHAPTER 2 GEOLOGIC OVERVIEW ....................................................................................... 8

2.1 Regional Structural Setting ............................................................................................. 10

2.2 Characteristics .................................................................................................................... 12

2.3 Stratigraphy .......................................................................................................................... 12

CHAPTER 3 COMPOSITIONAL CHARACTERISTICS ................................................................................ 14

3.1 Mineralogy ........................................................................................................................ 14

3.2 Facies .................................................................................................................................... 22

3.2.1 Facies 1: silica-rich argillaceous mudstone ................................................................. 22

3.2.2 Facies 2: mixed argillaceous mudstone ........................................................................ 23

3.2.3 Facies 3: foraminiferal to foram-rich mixed carbonate mudstone ......................... 24

3.2.4 Facies 4: silica-rich carbonate mudstone ...................................................................... 27
3.2.5 Facies 5: carbonate-dominated mudstone ............................................... 28
3.2.6 Facies 6: recrystallized carbonate limestone .......................................... 28
3.2.7 Facies 7: foraminiferal mixed carbonate mudstone .................................. 29
3.2.8 Facies 8: claystone ................................................................................... 31

CHAPTER 4 PALEONTOLOGY .................................................................................33
4.1 Foraminifera ........................................................................................................33
4.2 Echinoderms .........................................................................................................41
4.3 Bivalves .................................................................................................................41
4.4 Fish bones ..............................................................................................................41
4.5 Radiolaria ................................................................................................................41
4.6 Coccoliths ..............................................................................................................44
4.7 Calcispheres .........................................................................................................44

CHAPTER 5 PORE SYSTEM CHARACTERIZATION .............................................51
5.1 Quantitative analysis of porosity ........................................................................51
  5.1.1 Water immersion porosimetry (WIP) ............................................................. 51
  5.1.2 Mercury injection capillary pressure (MICP) ............................................... 53
5.2 Imaging study of pore types .................................................................................63
  5.2.1 Interparticle pores ........................................................................................ 64
  5.2.2 Intraparticle pores ....................................................................................... 64
  5.2.3 Intraparticle organic matter pores .............................................................. 69
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.4</td>
<td>Microfractures</td>
</tr>
<tr>
<td>CHAPTER 6</td>
<td>ORGANIC MATTER CHARACTERIZATION AND HYDROCARBON POTENTIAL</td>
</tr>
<tr>
<td>6.1</td>
<td>Self-contained source-reservoir system</td>
</tr>
<tr>
<td>6.2</td>
<td>Organic matter type and distribution</td>
</tr>
<tr>
<td>CHAPTER 7</td>
<td>CONCLUSIONS</td>
</tr>
<tr>
<td>CHAPTER 8</td>
<td>FUTURE WORK</td>
</tr>
<tr>
<td>LIST OF SYMBOLS AND ACRONYMS</td>
<td></td>
</tr>
<tr>
<td>REFERENCES CITED</td>
<td></td>
</tr>
<tr>
<td>APPENDIX A</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1 Location of Gonzales and La Salle counties. .......................................................... 3
Figure 2.1 Major structural and tectonic features in the region of the Eagle Ford play. ........ 9
Figure 2.2 Paleogeography reconstruction of North America during the Late Cretaceous. 10
Figure 2.3 Generalized stratigraphic column for the Late Cretaceous in the Central Texas area............................................................................................................ 13
Figure 3.1a Well #1 log showing part of the Buda Limestone, Eagle Ford Shale, and part of the Austin Chalk.......................................................... 15
Figure 3.1b Well #2 log showing part of the Buda Limestone, lower Eagle Ford, and part of the upper Eagle Ford.......................................................... 16
Figure 3.2a XRD bulk mineralogy of the Buda, lower and upper Eagle Ford, and Austin Chalk for Well #1 in Gonzales County ........................................ 18
Figure 3.2b XRD bulk mineralogy of lower Eagle Ford for Well #2 in La Salle County...... 18
Figure 3.3a Organic mudstones classification for the lower Eagle Ford................................ 20
Figure 3.3b Organic mudstones classification for the upper Eagle Ford............................. 20
Figure 3.4 SEM and corresponding QEMSCAN images of the Eagle Ford ..................... 21
Figure 3.5 Photomicrographs of silica-rich argillaceous mudstone facies ....................... 23
Figure 3.6 Photomicrographs of mixed argillaceous mudstone facies ............................. 25
Figure 3.7 Photomicrographs of mixed carbonate mudstone facies ............................... 26
Figure 3.8 Photomicrographs of silica-rich mudstone facies .......................................... 28
Figure 3.9 Photomicrographs of carbonate-dominated mudstone .............................. 29
Figure 3.10 Photomicrographs of neomorphized recrystallized limestone ...................... 30
Figure 3.11 Photomicrographs of mixed carbonate mudstone ....................................... 31
Figure 3.12 Photomicrographs of ash deposits ................................................................. 32
Figure 4.1 Morphologies and sections through foraminiferal tests. ................................. 34
Figure 4.2 Photomicrographs of single chambered foraminifera in thin section................. 35
Figure 4.3 Photomicrographs of multichambered uniserial foraminifera in thin section ..... 35
Figure 4.4 Photomicrographs of multichambered biserial foraminifera in thin section ..... 36
Figure 4.5 Photomicrographs of multichambered triserial foraminifera in thin section ..... 37
Figure 4.6 Photomicrographs of multichambered trochospiral foraminifera in thin section .................................................. 38
Figure 4.7a Photomicrographs of foraminifera with unidentified morphology in thin section .................................................. 39
Figure 4.7b Photomicrographs of foraminifera with unidentified morphology in thin section .................................................. 40
Figure 4.8 Photomicrographs of echinoderm plates and spines ............................................. 42
Figure 4.8 Photomicrographs of echinoderm plates and spines (continued) ..................... 43
Figure 4.9 Photomicrographs of bivalves .......................................................... 45
Figure 4.10 Photomicrographs of fish bones .......................................................... 46
Figure 4.11 Photomicrographs of radiolaria .......................................................... 47
Figure 4.12a SEM image of coccolith impressions .................................................. 48
Figure 4.12b SEM image of coccolith impressions .................................................. 48
Figure 4.13a SEM image of fecal pellet .......................................................... 49
Figure 4.13b SEM image showing coccoliths within the fecal pellet ......................... 49
Figure 4.14 SEM image of calxisphere .......................................................... 50
Figure 5.1 WIP results. ......................................................................................... 54
Figure 5.2 Scatter-plot of total porosity in WIP and measured total clays content in XRD .......................................................... 55
Figure 5.3 Scatter-plot of calculated total porosity in WIP and measured total carbonates content in XRD .......................................................... 55
Figure 5.4 Pore throat size histograms for the upper Eagle Ford, Well #1 .................. 57
Figure 5.5 Pore throat size histograms for the lower Eagle Ford, Well #1 .................. 58
Figure 5.6  Pore throat size histograms for the lower Eagle Ford, Well #2 .......................... 59
Figure 5.7  Cumulative pore throat diameter histogram......................................................... 60
Figure 5.8  MICP total porosity results.................................................................................. 61
Figure 5.9  Correlation between porosities obtained from MICP and WIP.......................... 62
Figure 5.10  MICP porosity vs MICP permeability................................................................. 63
Figure 5.11  Pore type classification in mudrocks................................................................. 65
Figure 5.12  SEM photomicrographs of interparticle pores .................................................... 66
Figure 5.13  SEM photomicrographs of intraparticle pores .................................................... 67
Figure 5.14  SEM photomicrographs of intraparticle pores .................................................... 68
Figure 5.15  Qualitative categorization of organic matter porosity ........................................ 69
Figure 5.16  Organic matter textures observed in organic rich shales................................. 70
Figure 5.17  SEM photomicrographs of intraparticle organic matter pores ............................ 71
Figure 5.18  SEM photomicrographs of intraparticle organic matter pores ............................ 72
Figure 5.19  SEM photomicrographs of intraparticle organic matter pores ............................ 73
Figure 5.20  SEM photomicrographs of intraparticle organic matter pores ............................ 74
Figure 5.21  SEM photomicrographs of intraparticle organic matter pores ............................ 75
Figure 5.22  SEM photomicrographs of intraparticle organic matter pores ............................ 76
Figure 5.23  Shrinkage microfractures observed on SEM....................................................... 77
Figure 5.24  Photomicrographs of Type I and Type II microfractures.................................... 79
Figure 5.25  Photomicrographs of Type I microfractures ....................................................... 80
Figure 5.26  Photomicrographs of Type I and Type II microfractures.................................... 81
Figure 6.1  Ramp of temperature settings for the Basic/Bulk-Rock, Shale Play and Reservoir methods ............................................................... 84
Figure 6.2  Pyrogram type obtained from the IFPEN Shale Play method............................ 85
Figure A.1e Sample #GZ-8 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 120

Figure A.1f Sample #GZ-9 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 121

Figure A.1g Sample #GZ-10 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 121

Figure A.1h Sample #LS-1 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 122

Figure A.1i Sample #LS-2 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 122

Figure A.1j Sample #LS-3 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 123

Figure A.1k Sample #LS-4 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 123

Figure A.1l Sample #LS-5 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot ................................................................. 124
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Calculated percentage increase in hydrocarbons quantification between Basic/Bulk-Rock method and Shale Play method.</td>
<td>90</td>
</tr>
<tr>
<td>A.1</td>
<td>XRD analysis results from Well #1 and Well #2 samples.</td>
<td>117</td>
</tr>
<tr>
<td>A.2</td>
<td>Water immersion porosimetry results from Well #1 and Well #2 samples.</td>
<td>117</td>
</tr>
<tr>
<td>A.3</td>
<td>MICP data and permeability results from Well #1 and Well #2 samples.</td>
<td>118</td>
</tr>
<tr>
<td>A.4</td>
<td>Rock-Eval results from Basic/Bulk-Rock method from Well #1 and Well #2 samples.</td>
<td>124</td>
</tr>
<tr>
<td>A.5</td>
<td>Rock-Eval results from IFPEN Shale Play method from Well #1 and Well #2 samples.</td>
<td>125</td>
</tr>
<tr>
<td>A.6</td>
<td>OIP intermediate calculations based on results obtained from Basic/Bulk-Rock method from Well #1 and Well #2 samples.</td>
<td>125</td>
</tr>
<tr>
<td>A.7</td>
<td>OIP intermediate calculations based on results obtained from IFPEN Shale Play method from Well #1 and Well #2 samples.</td>
<td>126</td>
</tr>
</tbody>
</table>
AKNOWLEDGEMENTS

I would like to acknowledge and thank my advisor Dr. Stephen A. Sonnenberg for his guidance during my graduate studies at Colorado School of Mines. His support, advice and technical expertise have tremendously contributed to broadening my scientific knowledge and improving my research skills. Moreover, I want to express my most sincere gratitude to Dr. Azra N. Tutuncu; she was always very supportive and open to exploring new ideas for my research work. I would also like to thank Dr. Donna Anderson and Dr. Michael Hendricks for their advice and time to read my research work.

Special thanks go to Compañía Española de Petróleos, S.A. (CEPSA) for fully funding my Master’s Degree, and to the members of the Unconventional Natural Gas and Oil Institute (UNGI) Coupled Integrated Multiscale Measurements and Modeling (CIMMM) Consortium for donating the cores and data used in this study.

In addition, I want to express my gratitude to the following people for their contribution to this research work: Dr. Anton Padin for all the collaborative petrographic work that we performed together; and Dr. Romero-Sarmiento from the IFPEN for analyzing my samples with the new Rock-Eval pyrolysis Shale Play method.

Last but not least, thank-you Vanessa, my life partner, for your patience, love and support during all this time in Colorado; and my family, especially my parents, for your effort towards my success.
CHAPTER 1
INTRODUCTION

The Eagle Ford Shale is the largest producing formation in the Gulf Coast region, South Texas (Figure 1.1). As of March 2016, oil and natural gas production surpassed 1.2 MMBOPD and 6.4 BCFPD respectively. These numbers make the Eagle Ford Region the second largest shale and tight oil producing region in the US, behind the Permian Region (2.0 MMBOPD) (EIA, 2016).

An important challenge when dealing with unconventional shale plays is how to maximize hydrocarbon production. In general, unconventional formations need to be hydraulically fractured to create high permeability pathways in the rock to allow the hydrocarbons to flow to the wellbore. Proper petrographic and petrophysical characterization can help to better identify sweestpots, and therefore to be more selective when targeting intervals for hydraulic fracturing a well (Kale et al., 2010).

Distinguishing between upper and lower Eagle Ford members can be very difficult. Seven stratigraphic intervals can be recognized and mapped within the Eagle Ford Shale between the San Marcos Arch and the Maverick Basin (Breyer et al., 2013), making the aforementioned distinction more difficult. In some parts of the Eagle Ford play area, gamma-ray logs show very clearly where the contact between upper and lower Eagle Ford is, whilst in others the contact is not that obvious. Therefore, additional petrographic and petrophysical techniques and methods are necessary to differentiate between both members and to be more selective in terms of identifying and evaluating the best well interval(s) to be hydraulically fractured.

The lower Eagle Ford is the interval that most companies target for hydrocarbon production. Nonetheless, the upper Eagle Ford might also be a member with great potential in
terms of hydrocarbon content (e.g., oil-in-place). One of the main objectives of this research work is to study the potential of the upper Eagle Ford based on the available core samples. Different methods and techniques were integrated to provide an accurate characterization and evaluation of this member. The lower Eagle Ford has also been studied to better understand the compositional and structural variability of this member at two well locations within the Eagle Ford play area.

1.1 Study area

The study area for this research is the Eagle Ford Shale in South Texas, located in the Gulf Coast region. More specifically, this research work is focused on Gonzales (Well #1) and La Salle (Well #2) counties (Figure 1.1). Gonzales County, considered part of the northern region of the Eagle Ford play, covers an area of 1,070 mi$^2$. The activity in this county is focused on the shale oil window, where the southwest portion presents greater potential. The most active operator in this county is EOG Resources. La Salle County is at the center of development of the Eagle Ford Shale, covering an area of 1,494 mi$^2$. In this county, the geology of the Eagle Ford Shale is very variable. As a result, production in this area includes oil, gas-condensate, wet gas and dry gas. Gas production increases towards the south and liquids production increases in the northern half of the county. The most active operators in this county are EOG Resources and Petrohawk (Eagle Ford Shale, 2016).

1.2 Objective

The main objective of this research work is to provide with an accurate characterization of the upper and lower Eagle Ford members at different locations within the Eagle Ford Shale play area. This will help to better understand the geological variability at microscopic scale and
petrophysical properties of the formation between two well locations. Based on this characterization, target intervals with the most potential in terms of oil content were identified.

Figure 1.1 Location of Gonzales (#1) and La Salle (#2) counties. From Texas Railroad Commission (2016).
In order to accomplish the main objectives stated above, well log interpretation, mineralogy, organic matter, paleontology, and pore system characterization are covered and integrated in a later interpretation of the obtained results.

1.3 Dataset and methodology

The analyses and methods used for this research are: 1) well log analysis; 2) transmitted light microscopy; 3) X-Ray Diffraction (XRD) analysis; 4) quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN); 5) Rock-Eval pyrolysis; 6) field emission scanning electron microscopy (FE-SEM) in Ar-ion milled samples; 7) environmental scanning electron microscope (ESEM) in both Ar-ion milled and broken samples; 8) mercury injection capillary pressure (MICP); and 9) water immersion porosimetry (WIP).

The available cores for this research correspond to two wells drilled in Gonzales (Well #1) and La Salle (Well #2) counties (well names excluded for proprietary reasons). Digital well-logs and cores were donated to the Colorado School of Mines Unconventional Natural Gas and Oil Institute (UNGI) Coupled Integrated Multiscale Measurements and Modeling (CIMMM) consortium by Hess Corporation. The available core and well data collected and sampled from Well #1 (samples #GZ) and Well #2 (samples #LS) are summarized below:

- Gamma-ray log
- Thin sections - 1 ft core interval sampling
- XRD - 1 ft interval core sampling
- QEMSCAN - 1 ft interval sampling
- Rock-Eval Pyrolysis - 1 ft core interval sampling
- FESEM - Ar-ion milled samples every 1 ft core interval
- ESEM - Ar-ion milled and broken surface samples every 1 ft core interval
- MICP - 1 ft core interval sampling
- WIP - 1 ft core interval sampling

Note that the Eagle Ford Shale characteristics at millimeter scale are highly variable. Therefore, all samples were prepared from exactly the same core depth to avoid any potential biased results.

Preliminary well-log interpretation based on gamma ray logs was performed to identify boundaries between Buda Limestone, lower Eagle Ford, upper Eagle Ford, and Austin Chalk. The spectral gamma-ray log recorded the elements thorium, uranium and potassium. The Techlog Wellbore Software Platform (Schlumberger Software) was used to perform this preliminary assessment.

Mineralogy identification and distribution, and facies characterization was then performed using XRD and QEMSCAN analysis. XRD analysis is a destructive method that provides an accurate mineral weight percentage composition of the whole rock sample. The samples were sent to The Mineral Lab (Golden, CO) for XRD analysis. QEMSCAN is a destructive method that provides a mineral percentage composition and visual distribution of a sample area. QEMSCAN was performed at Colorado School of Mines labs. In addition, a visual inspection of petrographic thin sections and rock samples on scanning electron microscopy (SEM) was carried out for mineral characterization and distribution in the available core samples.

Paleontology study of the Eagle Ford Shale was carried out by combining SEM and transmitted light microscopy. Microfossils, and more specifically foraminifera, are good paleodepth indicators (Douglas, 1983). The identification of these microfossils helped to
characterize facies and to better understand the fluctuation of the oxygen level during deposition of both the upper and lower Eagle Ford members.

A proper characterization of the pore system is important for determining oil and/or gas storage capacity in a rock. Different methods exist to quantitatively understand the pore structure (Kuila, 2013). For this research, a combination of MICP and WIP was performed to quantitatively characterize total porosity, pore throat size and pore size distribution in the available core samples. The samples were sent to Poro-Technology (Kingwood, TX) for MICP analysis. WIP was performed at Colorado School of Mines labs. Pore system characterization was coupled with visual pore classification using SEM images obtained from both Ar-ion milled and broken surface samples.

Microfractures were present in most Ar-ion milled samples observed on SEM. Whether these microfractures are induced or natural is very difficult to determine. Therefore, transmitted light microscopy was carried out along with SEM analysis to determine the abundance of naturally occurring microfractures in the Eagle Ford Shale.

The analysis used to evaluate the hydrocarbon potential of each group in this research is Rock-Eval pyrolysis. Two methods were used to better quantify the oil-in-place present in the rock: 1) Basic/Bulk-Rock method, where the shale rock is considered as the source rock only; and 2) the IFPEN Shale Play method for characterization of unconventional shale resource systems developed by the Institut Français du Pétrole Energies Nouvelles (IFPEN). This new method helped to better quantify the free or sorbed hydrocarbons in unconventional shale plays (Romero-Sarmiento et al., 2015). The available rock samples were sent to the IFPEN (France) to perform Rock-Eval pyrolysis.
Rock-Eval pyrolysis and SEM were the methods used to characterize the kerogen type and maturation, and to determine the organic matter distribution in the available core samples. Rock-Eval pyrolysis quantified the total organic carbon (TOC) and evaluation of the petroleum-generative potential and thermal maturity (Peters, 1986) of the core samples used for this research. This characterization was supported with visual characterization of detrital organic matter (DOM) and secondary organic matter (SOM) on core samples by using SEM.

FE-SEM and ESEM analyses and preparation of Ar-ion milled samples were performed at Colorado School of Mines labs. Rock samples were sent to Wagner Petrographic (Lindon, UT) for preparation of thin sections. These were prepared according to the following specifications:

- 20 µm thickness
- Double polished with cover glass. Some of the thin sections were also prepared without cover glass for SEM and QEMSCAN analyses.
- Red epoxy vacuum impregnation
- Grinded in oil
CHAPTER 2
GEOLOGIC OVERVIEW

The Eagle Ford Shale is a Late Cretaceous organic-rich marine mudrock primarily composed of carbonate and siliciclastic materials, with variable content in clay and other accessory minerals (Dawson, 2000; Driskill et al., 2012; Tian et al., 2012; Hart et al., 2013). It is located in South Texas, in the Gulf Coast region. The Eagle Ford Shale extends from the East Texas Basin in its northeastern limit to the Mexico Border in its south western part, covering an area of about 56,000 mi². The depth at which it is found ranges between 5,000 ft and 11,500 ft (Luneau et al., 2011), and it crops out irregularly in the northeast side of the Maverick Basin and southwest of the East Texas Basin. The Eagle Ford play area is bounded by the Stuart City and Sligo shelf margins to the south, and the Ouachita front to the north (Condon and Dyman, 2006; Hentz and Ruppel 2011) (Figure 2.1).

The Eagle Ford Shale was deposited in the Late Cretaceous in a marginal to open marine setting (Pessagno, 1969; Stehli et al., 1972; Surles, 1987, Dawson and Almon, 2010). The deposition occurred during eipiric sea transgression periods in western North America, more specifically in the southern part of the Western Interior Seaway (WIS) (Robison, 1997) (Figure 2.2). Deposition began during Middle Cenomanian and lasted until the Late Turonian (Wehner et al., 2015). During this period of time, other important Cretaceous organic-rich mudrocks were also deposited along the WIS in North America, such as the Mowry, Graneros and Greenhorn shales (Dawson, 2000).

The Eagle Ford Shale presents a singularity compared to other unconventional plays in the US, such as the Haynesville, Barnett and Marcellus: it crops out at numerous surface locations, offering the opportunity to understand the facies variability and lateral heterogeneities
of the formation at different scales, as well as to characterize other important geologic features such as biostratigraphy. Outcrops can be observed in highway exposures in Val Verde and Terrell counties, Texas. Good quality outcrops can also be found in canyon systems draining into the Rio Grande in Val Verde, Terrell and Brewster counties. In these western Texas counties, the Eagle Ford Shale outcrop is also referred to as the Boquillas Formation (Donovan and Staerker, 2010; Donovan et al., 2013).

Figure 2.1   Major structural and tectonic features in the region of the Eagle Ford play. From EAI (2014).
2.1 Regional Structural Setting

Extensional tectonic events initiated a rifting period that continued from the Late Triassic until the Late Jurassic in northeastern Mexico. This rifting event is associated with the opening of the Gulf of Mexico. Several shallow-marine shelf areas developed in the region as a result of slow but continuous subsidence of the area accompanied by sedimentation. The creation of accommodation space allowed carbonate materials to accumulate and subsequently to develop carbonate platforms during Early Cretaceous time (Lehman et al., 1999; Montgomery et al., 2002; Mancini et al., 2008).

Figure 2.2 Paleogeography reconstruction of North America during the Late Cretaceous, including locations for the WIS and Eagle Ford play area. Adapted from Blakey (1994).
The Comanche Platform is present over much of Central Texas. It developed during Albian and Early Cenomanian time on the top of Jurassic ramp sediments (Gardner et al., 2013, Phelps et al., 2014). Similar to other carbonate platforms in northern Gulf of Mexico, the Comanche Platform is composed of a succession of prograding, individual carbonate platforms alternating with transgressive deep marine facies, such as shales or sandstones (Montgomery et al., 2002). The Comanche Platform presents two characteristic primary depositional profiles: 1) flat-topped reef-rimmed platforms driven by biotic processes and formed during regressive episodes, and 2) storm-dominated ramp profiles driven by physical processes and formed during transgressive episodes (Harbor, 2011). Episodes of rapid marine transgression and deposition of organic-rich mudstones coincided with back-stepping of the Comanche Platform. The Pearsall (Pine Island and Bexar members), Del Rio and Eagle Ford were deposited during one of these platform-inundation episodes, where the Eagle Ford is the thickest deposit. The margin of the Maverick Basin and the East Texas Basin are considered the main depocenters where primary deposition happened (Harbor, 2011; Workman, 2013).

The Eagle Ford was deposited during the Middle to Late Cenomanian eustatic transgression of the Comanche Shelf and lies on top of one of the major Mesozoic-time discontinuities of the Gulf of Mexico (Dawson, 1997; Harbor, 2011). This discontinuity, considered as an exceptional drowning unconformity example, is well recognized in seismic profiles and is named by several authors as the mid-Cretaceous unconformity (MCU) (Winker and Buffler, 1988; Faust, 1990; Dawson, 1997; Galloway, 2008). The MCU resulted as a combination of various events, including tectonic uplift and tilting of the San Marcos Arch, Sabine uplift, and Monroe uplift and subsequent subaerial erosion. The tectonic uplift generated new source areas that eroded and provided an influx of siliciclastic detritus transported by fluvial
systems that occurred for around 8 Ma. Alluvial, deltaic, and coastal depositional systems developed in the region, thus switching from a carbonate platform to a ramp profile (Galloway, 2008, Harbor, 2011).

2.2 Characteristics

The Eagle Ford Basin was partially filled with siliciclastic detritus delivered from deltas prograding southwestward. Regionally, the depositional system is characterized by a mixture of siliciclastic and bioclastic materials. The more proximal lithofacies, deposited on a shallow shelf, are composed of laminated organic-rich shales, alternating with carbonaceous quartzose siltstones and bioclastic limestones. In contrast, the more distal lithofacies are composed of organic-rich shales alternating with bioclastic limestones, and phosphatic shales and graded siltstones. Distal lithofacies were primarily deposited in oxygen-poor conditions based on the presence of authigenic pyrite and limited bioturbation. Nonetheless, the presence of benthonic fauna indicates that there were deposition periods where oxygen levels were higher (Dawson and Almon, 2010).

2.3 Stratigraphy

The Eagle Ford Shale was deposited during the Late Cretaceous (Cenomanian to Turonian) as a result of a global marine transgression in Western North America. It disconformably underlies the Austin Chalk and unconformably overlies the Buda Limestone on the western side of the San Marcos Arch (Figure 2.3). On the eastern side of the San Marcos Arch, the Eagle Ford Shale disconformably overlies the Woodbine Group (Dawson, 1997). The Eagle Ford Shale is considered to be the source rock for the Austin Chalk, which was first drilled for oil in the 1920s (Doyle, 1955). The contact between the Eagle Ford and the Austin Chalk
represents the Turonian/Coniacian boundary (89 Ma) which is recognized in outcrops by the presence of a significant unconformity (Dawson, 2000).

Two major depositional units are recognized within the Eagle Ford: an oil-prone transgressive unit (lower Eagle Ford) and a gas-prone regressive unit (upper Eagle Ford) (Dawson and Almon, 2010). From inversion data results, the upper Eagle Ford and lower Austin Chalk together constitute a continuous unconventional hydrocarbon play (Ogiesoba, 2014). The Cenomanian/Turonian boundary occurs within the lower and the upper Eagle Ford boundaries (92 Ma) (Dawson, 2000; Donovan and Staerker, 2010).
CHAPTER 3
COMPOSITIONAL CHARACTERISTICS

This chapter aims to provide a description of the mineralogical composition and distribution of the Eagle Ford at Well #1 and Well #2 locations based on XRD and QEMSCAN analyses. A petrography study based on reflected light microscopy has also been carried out to describe the different facies found at both the upper and lower Eagle Ford. The facies classification is based on microfossil abundance and mineralogical composition of the samples.

As an introduction to the compositional characterization of the Eagle Ford, gamma-ray logs for Well #1 and Well #2 are shown in Figure 3.1a and Figure 3.1b respectively. The gamma-ray response is generally lower in the upper Eagle Ford. Nonetheless, there can be carbonate-rich intervals within the lower Eagle Ford. At these levels, the gamma-ray response will be similar in both members. The gamma-ray data has been split into thorium (Th), uranium (U) and potassium (K) for both wells. As a preliminary screening process, the content in thorium can be used to differentiate between upper and lower Eagle Ford within the same well. In general, the lower Eagle Ford presents higher thorium content compared to the upper Eagle Ford. Also, the lower Eagle Ford at Well #2 location presents less thorium concentration compared to the same member at Well #1. This higher content in thorium is due not only to a higher content in clays, but more specifically to a higher content of kaolinite (Hancock, 1993).

3.1 Mineralogy

The Eagle Ford Shale has very fine-grain size constituents and therefore a visual estimation of the mineralogy is very inaccurate. XRD and QEMSCAN were carried out in the available core samples to determine the mineralogy composition and distribution of the rock.
Figure 3.1a  Well #1 log showing part of the Buda Limestone, Eagle Ford Shale, and part of the Austin Chalk. Track 1: gamma ray (0-200 GAPI); track 2: thorium (0-16 ppm); track 3: uranium (0-20 ppm); and track 4: potassium (0-3 %). Depth scale 1:250 ft.
Figure 3.1b Well #2 log showing part of the Buda Limestone, lower Eagle Ford, and part of the upper Eagle Ford. Track 1: gamma ray (0-200 GAPI); track 2: thorium (0-16 ppm); track 3: uranium (0-20 ppm); and track 4: potassium (0-3 %). Depth scale 1:250 ft.
Mineralogy of the Eagle Ford Shales has been analyzed using XRD, a destructive method that provides an accurate mineral weight percentage (wt. %) composition of the whole rock samples. Well #1 is nearby the San Marcos Arch area, in Gonzales County. At this location, the lower Eagle Ford is primarily composed of quartz, mica/illite and kaolinite. K-Feldspar and pyrite are present as secondary minerals. For the same well, upper Eagle Ford consists of carbonate-dominated mineralogical composition, where calcite is the main carbonate component followed by quartz and mica/illite. Dolomite, kaolinite, plagioclase, chlorite and pyrite may be present as secondary minerals. Two of the analyzed samples illustrate a very different mineralogical composition in the upper Eagle Ford. Sample #GZ-7’ is primarily composed of calcite. Quartz, plagioclase and pyrite are present as secondary minerals. This sample corresponds to a neomorphic recrystallized limestone as will be described in the following sections. Sample #GZ-6’ is primarily composed of mica/illite, followed by plagioclase, kaolinite and pyrite, and an amorphous material that could not be identified by XRD analysis. This sample corresponds to volcanic ash that will be described in the following section. The XRD results for Well#1 are represented in Figure 3.2a.

Well#2 is located 100 miles away southwest from Well#2, in La Salle County. At this location, the lower Eagle Ford shows a different composition than the same member at Well #1. It is primarily composed of calcite, followed by quartz and mica/illite. Dolomite, kaolinite, plagioclase and pyrite may be present as secondary minerals (Figure 3.2b).

Many different mudrock classification diagrams exist in the literature (Dunn et al., 2012; Passey et al., 2010; Passey et al., 2012; Allix et al., 2010; Macquaker and Adams, 2003). Based on the available data and nature of the rock, the ‘sCore’ classification for organic mudstone (Gamero-Diaz et al., 2012) has been considered the most suitable for this research. The results
Figure 3.2a  XRD bulk mineralogy of the Buda, lower and upper Eagle Ford, and Austin Chalk for Well #1 in Gonzales County, Texas.

Figure 3.2b  XRD bulk mineralogy of lower Eagle Ford for Well #2 in La Salle County, Texas.
obtained from XRD were plotted on this classification. The lower Eagle Ford at Well #1 location plots in two different organic mudstone lithofacies: 1) mixed siliceous mudstone; and 2) clay-rich siliceous mudstone. At Well #2 location, the lower Eagle Ford plots in three different organic mudstone lithofacies: 1) mixed carbonate mudstone; 2) silica-rich mudstone; and mixed mudstone (Figure 3.3a). Upper Eagle Ford (Well #1) plots in three different organic mudstone lithofacies: 1) carbonate-dominated lithotype; 2) mixed carbonate mudstone; and 2) silica-rich argillaceous lithotype (Figure 3.3b).

QEMSCAN images show the differences in mineralogical distribution between the lower and upper Eagle Ford, and between Well #1 and Well #2 for the lower Eagle Ford (Figure 3.4). Lower Eagle Ford at Well #1 consists of a quartz and clay-rich matrix. Numerous pyrite framboids are observed and dispersed throughout the matrix. Carbonate minerals are associated with microfossils tests and bioclastic fragments. In contrast, the lower Eagle Ford at Well #2 consists of a completely different mineralogical composition and distribution. This member is clearly carbonate dominated. Calcite is either present in the microfossil test composition or forming carbonate aggregates in the matrix. Clays are preferentially present inside the fossils or in the intergranular space between carbonate grains and aggregates. Pyrite is less abundant and rarely forms framboids compared to the lower Eagle Ford in Well #1. The upper Eagle Ford is also carbonate-dominated, where calcite is the primary carbonate mineral. The matrix is very rich in calcite, and clays are restricted to the available intergranular space. Pyrite is present most likely as a result of pyritization processes of other minerals. Quartz is present in the intergranular space, presumably associated with organic matter.
Figure 3.3a Organic mudstones classification for the lower Eagle Ford at different well locations. Adapted from Gamero et al. (2012).

Figure 3.3b Organic mudstones classification for the upper Eagle Ford at Well #1 location. Adapted from Gamero et al. (2012).
Figure 3.4  SEM (left) and corresponding QEMSCAN (right) images of the lower Eagle Ford, sample #LS-5, Well #2; lower Eagle Ford, sample #GZ-9, Well #1; and upper Eagle Ford, sample #GZ-5, Well #1. The oval-shape calcite aggregates oriented parallel to lamination correspond to fecal pellets in the lower Eagle Ford, Well #2. The brightest spots on SEM images correspond to pyrite grains.
3.2 Facies

Eight Eagle Ford Shale facies have been recognized based on XRD data, and petrographic thin sections under transmitted light microscopy: 1) silica-rich argillaceous mudstone; 2) mixed argillaceous mudstone; 3) foraminiferal to foram-rich mixed carbonate mudstone; 4) silica-rich carbonate mudstone; 5) carbonate-dominated mudstone; 6) recrystallized carbonate limestone; 7) foraminiferal mixed mudstone; and 8) claystone. Most of these facies are not restricted to a unique member of the Eagle Ford and are present at multiple depths. This indicates the changes in the depositional environment, leading to repeated, interstratified depositional facies. In order to make a more exhaustive facies description, microfacies have also been identified and described below when present.

3.2.1 Facies 1: silica-rich argillaceous mudstone

Facies 1 is a silica-rich argillaceous mudstone with average TOC content of 2.71 wt. %. This facies is composed of two microfacies, 1a and 1b, interstratified with microfacies 2a. These microfacies are separated by non-transitional boundaries as shown in Figure 3.5.

Microfacies 1a exhibits a loosely to densely packed fabric characterized by abundant microfossils. It is rich in pyrite (20 %) and microfossils (40 %), most of them moderately-preserved foraminifera. The test chambers of foraminifera are cemented with calcite. This microfacies presents tabular, well developed detrital clays. Most authigenic pyrite crystals are euhedral with sizes of up to 0.4 mm.

Microfacies 1b shows wavy lamination and exhibits a dispersed to loosely packed fabric. It is rich in carbonate bioclasts (25 %) from bivalves and other unidentified microfossils. Foraminifera, when present, are well-preserved with their test chambers cemented with calcite. Fecal pellets are well-preserved or deformed due to compaction around carbonate aggregates and
bioclasts. The presence of flattened burrows indicates bioturbation activity within this microfacies.

Figure 3.5 Photomicrographs of silica-rich argillaceous mudstone facies. (A) Photomicrograph of facies 1 showing the contact between microfacies (black arrows). Plane polarized light. 2.5x magnification. Lower Eagle Ford, sample #GZ-10, Well #1. (B) Photomicrograph of microfacies 1a. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #GZ-10, Well #1. (C) Photomicrograph of microfacies 1b showing wavy lamination due to compaction around aggregates of carbonate bioclasts. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #GZ-10, Well #1.

3.2.2 Facies 2: mixed argillaceous mudstone

Facies 2 is a mixed argillaceous mudstone with average TOC content of 2.33 wt. %. This lithofacies consists of two different microfacies: 2a and 2b (Figure 3.6). The boundary between both microfacies is recognized by a non-transitional change in color, composition and
lamination. This non-transitional change between both microfacies indicates a change in the depositional environment.

Microfacies 2a is finely laminated and exhibits a dispersed fabric where microfossils are floating throughout the matrix. Presence of microfossils is less than 5%, although at some levels it can be up to 15%. The microfossils present in this microfacies are well preserved foraminifera with their test chambers cemented with calcite. Fragments of carbonate bioclasts are abundant. Silt-size quartz grains are dispersed throughout the matrix. These grains are very angular and very well preserved indicating a detrital origin and a relative proximity to the source area. Presence of fecal pellets and signs of bioturbation is rare within this microfacies.

Microfacies 2b ranges from finely laminated to wavy laminated. The wavy lamination is the result of compaction around bioclastic materials. It shows a dispersed to densely packed fabric. Silt-size very angular quartz grains are dispersed throughout the matrix. The microfossils present in this microfacies (approximately 15%) are mostly well preserved foraminifera floating within the matrix or forming thin carbonate lenses. Foraminifera test chambers are cemented with calcite. The content in carbonate bioclastic materials is abundant and similar to microfacies 1a. Organic-rich fecal pellets are abundant and well preserved, although some of them show deformation due to compaction.

3.2.3 Facies 3: foraminiferal to foram-rich mixed carbonate mudstone

Facies 3 is a mixed carbonate mudstone with average TOC of 6.34. This facies is composed of two microfacies, 3a and 3b (Figure 3.7). The main difference between these two microfacies is the fossil abundance and type.
Figure 3.6 Photomicrographs of mixed argillaceous mudstone facies. (A) Photomicrograph of facies 2 showing the contact between microfacies 2a and 2b (black arrows). Plane polarized light. 2.5x magnification. Lower Eagle Ford, sample #GZ-9, Well #1. (B) Photomicrograph of microfacies 2a showing silt-size quartz and organic matter aggregates. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #GZ-9, Well #1. (C) Photomicrograph of microfacies 2b illustrating foraminifera carbonate lenses within the organic and clay-size mudrock matrix. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #GZ-9, Well #1.
Figure 3.7 Photomicrographs of foraminiferal to foram-rich mixed carbonate mudstone facies. (A) Photomicrograph of microfacies 3a showing limestone concretions. Plane polarized light. 2.5x magnification. Lower Eagle Ford, sample #LS-1, Well #2. (B) Photomicrograph of microfacies 3a showing foraminifer tests filled with organic matter and kaolinite, and with calcite cement. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #LS-1, Well #2. (C) Photomicrograph of microfacies 3b illustrating the abundance in microfossils compared to microfacies 3a. Plane polarized light. 2.5x magnification. Lower Eagle Ford, sample LS-5, Well #2. (D) Photomicrograph of microfacies 3b identifying echinoderm spines and plates, and foraminifera with their test chambers filled with kaolinite and organic matter. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #LS-5, Well #2.
Microfacies 3a is wavy laminated and shows a loosely packed fabric characterized by abundant well-to moderately preserved microfossils. It is rich in foraminifera (30 %) and other carbonate bioclastic fragments, including echinoderm plates. The foraminifera have test chambers either cemented with calcite or filled with a mixture of kaolinite and organic matter. Some of the test chambers collapsed during compaction, especially those filled with kaolinite and organic matter. This compaction also affected to fecal pellets and burrows. At some levels, this microfacies is interstratified with limestone concretions of less than 0.5 mm thick. These carbonate concretions are composed of foraminifera, echinoderm plates and other carbonate bioclastic fragments.

Microfacies 3b ranges from finely laminated to lenticular laminated and exhibits a densely packed fabric characterized by abundant microfossils. It is mainly composed of foraminifera (35 to 50 %) and other carbonate bioclastic fragments, such as echinoderm plates and spines. Within this microfacies, foraminifera and echinoderm spines and predominantly filled with organic matter and kaolinite. Most fecal pellets are flattened and deformed. Similar to microfacies 3a, there are some levels at which the mudstone is interstratified with limestone concretions. These concretions are composed of carbonate microfossils and bioclastic fragments.

3.2.4 Facies 4: silica-rich carbonate mudstone

Facies 4 is a bituminous silica-rich carbonate mudstone with average TOC of 7.28 wt. %. It is finely laminated to wavy laminated and exhibits a dispersed fabric characterized by the presence of microfossils floating throughout the matrix. Microfossils content is in general less than 15%, where foraminifera are dominant. Similar to microfacies 3b, the test chambers of foraminifera are filled with kaolinite and organic matter. Silt-size quartz and other carbonate
bioclastic fragments are dispersed throughout the matrix. Fecal pellets are well-preserved although some of them may be flattened due to compaction (Figure 3.8).

![Figure 3.8 Photomicrographs of silica-rich carbonate mudstone facies. (A) Photomicrograph of facies 4 illustrating the lamination of the mudrock. Plane polarized light. 2.5x magnification. Lower Eagle Ford, sample #LS-2, Well #2. (B) Photomicrograph of facies 4 showing foraminifera tests filled with organic matter. Note the very angular silt-size quartz grains. Plane polarized light. 10x magnification. Lower Eagle Ford, sample #LS-2, Well #2.]

3.2.5 Facies 5: carbonate-dominated mudstone

Facies 5 is a carbonate-dominated mudstone with average TOC of 1.65 wt. %. It does not present any preferential lamination and shows a dispersed to loosely packed fabric. Carbonate laminae concretions are present at some levels. These laminae are composed of foraminifera and small carbonate bioclastic fragments. Very well preserved foraminifera are present within this microfacies. The test chambers of foraminifera are cemented with calcite, some of them partially pyritized. Well preserved echinoderm plates and bivalves fragments are also frequent within this microfacies. Microfossil content is approximately 15 % (Figure 3.9).

3.2.6 Facies 6: recrystallized carbonate limestone

Facies 6 is a recrystallized limestone where the preexisting intergranular pores were filled with sparry calcite in some areas. Recrystallization does not imply change in mineralogy.
Instead, this process is associated with a change in size, shape and lattice of the crystal (Flügel, 2004). Calcispheres, foraminifera and radiolarians are abundant within this lithofacies as part of the fabric. Most radiolarians are partially recrystallized, where the siliceous tests are replaced by calcite. Coarse sparry calcite crystals are the result of recrystallization of fine lime mud. Relicts of former round micritic peloids are also abundant in this facies (Figure 3.10).

Figure 3.9 Photomicrographs of carbonate-dominated mudstone. (A) Photomicrograph of facies 5. Plane polarized light. 2.5x magnification. Upper Eagle Ford, sample #GZ-4, Well #1. (B) Photomicrograph of facies 5 showing foraminifera, bivalves fragments and phosphatic bioclasts. Plane polarized light. 10x magnification. Upper Eagle Ford, sample #GZ-4, Well #1.

3.2.7 Facies 7: foraminiferal mixed mudstone

Facies 7 is a mixed mudstone with average TOC of 7.96 wt. %. This facies shows planar to wavy lamination and exhibits predominantly dispersed fabric, although it can be loosely to densely packed at some parts. There are some condensate levels with high content in large size fossils such as fish bones and inoceramids, and other carbonate and phosphatic clasts. Microfossil content is around 15 % and it is very diverse. Fecal pellets and burrows are abundant and deformed as a result of compaction (Figure 3.11).
Figure 3.10 Photomicrographs of recrystallized limestone. (A) Photomicrograph of lithofacies 6 showing small-size calcispheres and recrystallized radiolaria. Plane polarized light. 10x magnification. (B) Same photomicrograph under cross polarized light. 10x magnification. (C) Photomicrograph of facies 6 showing the relicts of peloids. Note the secondary (migrated) organic matter (e.g., bitumen, pyrobitumen, solid bitumen) filling the intergranular pore space. Plane polarized light. 10x magnification. (D) Same photomicrograph under cross polarized light. Note the large sparry-calcite crystals. 10x magnification. Upper Eagle Ford, sample #GZ-7’, Well #1.
3.2.8 Facies 8: claystone

Facies 8 represents wind-blown ash deposits associated with volcanism. The contact between the ash deposits and the previously deposited sediments is sharp and abrupt as a result of the high energy event. As expected, this facies is massive, without any preferential lamination. Rectangular-shaped crystals of different sizes, probably plagioclase, are dispersed in the matrix (Figure 3.12).
Figure 3.12 Photomicrographs of ash deposits. (A) Photomicrograph showing the boundary with preexisting sediments (white arrows). Plane polarized light. 10x magnification. (B) Close-up photomicrograph of A, showing well-developed crystals within the volcanic ash. Plane polarized light. 2.5x magnification. Upper Eagle Ford, sample #GZ-6’, Well #1.
CHAPTER 4
PALEONTOLOGY

The Eagle Ford Shale is very rich in calcareous microfossils, where foraminifera are dominant. For the purpose of identifying different types of fossils, a paleontological imaging study has been carried out by using transmitted light microscopy and SEM on thin sections and core samples from Well #1 and Well #2.

Microfossils, and more specifically foraminifera, are good paleodepth indicators (Douglas, 1983). Microfossils abundance within the lower Eagle Ford at Well #1 is very low compared to the upper Eagle Ford, Well #1, and lower Eagle Ford, Well #2. This difference in fossil abundance indicates that the lower Eagle Ford at Well #1 location was presumably deposited under lower oxygen level conditions. The fossils recognized in the available samples are: 1) foraminifera, 2) echinoderms, 3) bivalves, 4) fish bones, 5) radiolaria, 6) coccoliths and 7) calcispheres.

4.1 Foraminifera

The foraminifera are a very diverse group of marine protozoans that can be present in all marine environments (Kennett, 1982). They are classified in benthonic and planktonic families, where the first is the least abundant. From about 4,000 modern species, only 40 species correspond to benthonic foraminifera. Planktonic foraminifera live in the upper 300 m of the water column where food supply is larger compared to deeper sea-levels. In contrast, benthonic foraminifera live along and beneath the seafloor (Scholle and Ulmer-Scholle, 2006). In general, the size of these fossils ranges from less than 0.1 mm to 1 mm, although some groups may be larger (up to 20 cm in length). The skeleton of planktonic foraminifera consists of shell chambers primarily made of calcite. These chambers are originally void and represent potential pore spaces
Foraminifera can be classified depending on their test morphology as: 1) single chambered, 2) multichambered uniserial, 3) multichambered biserial, 4) multichambered planspiral, 5) multichambered triserial and 6) multichambered trochospiral (Figure 4.1). From thin sections, single chambered (Figure 4.2), multichambered uniserial (Figure 4.3), multichambered biserial (Figure 4.4), multichambered triserial (Figure 4.5) and multichambered trochospiral (Figure 4.6) morphologies have been recognized in the available samples. Other unidentified morphologies are shown in Figure 4.7a and Figure 4.7b.

Figure 4.1 Morphologies and sections through foraminiferal tests. Modified from Flügel (2004).
Figure 4.2 Photomicrographs of single chambered foraminifera in thin section. The test chambers are cemented with calcite. Plane polarized light. 40x magnification. Upper Eagle Ford, sample #GZ-4, Well #1.

Figure 4.3 Photomicrographs of multichambered uniserial foraminifera in thin section. The test chambers are cemented with calcite in A, B, and D. Plane polarized light. Photomicrographs A (20x magnification), B (40x magnification) and C (40x magnification) correspond to upper Eagle
Ford, sample #GZ-4, Well #1; photomicrograph D (20x magnification) corresponds to upper Eagle Ford, sample #GZ-5, Well #1.

Figure 4.4 Photomicrographs of multichambered biserial foraminifera in thin section. The test chambers are cemented with calcite in A, B, C and D, and filled with a mixture of organic matter and kaolinite in E. Plane polarized light. Photomicrographs A (20x magnification), B (40x magnification) and C (40x magnification) correspond to upper Eagle Ford, sample #GZ-4, Well #1; photomicrograph D (20x magnification) corresponds to lower Eagle Ford, sample #LS-3,
Well #2; photomicrograph E (20x magnification) corresponds to lower Eagle Ford, sample #LS-4, Well #2.

Figure 4.5  Photomicrographs of multichambered triserial foraminifera in thin section. The test chambers are cemented with calcite in A, B and C, and filled with a mixture of organic matter and kaolinite in D. Plane polarized light. Photomicrographs A (20x magnification), B (20x magnification) and C (20x magnification) correspond to upper Eagle Ford, sample #GZ-4, Well #1; photomicrograph D (20x magnification) corresponds to lower Eagle Ford, sample #LS-2, Well #2.
Figure 4.6 Photomicrographs of multichambered trochospiral foraminifera in thin section. The test chambers are cemented with calcite in A, and filled with a mixture of organic matter and kaolinite in C. (A) Multichambered trochospiral benthonic foraminifera under plane polarized light. 20x magnification; (B) Same photomicrograph under cross polarized light. Lower Eagle Ford, sample #LS-5, Well #2. (C) Equatorial section of trochospiral foraminifera. Plane polarized light. 20x magnification. Lower Eagle Ford, sample #LS-1, Well #2.
Figure 4.7a Photomicrographs of foraminifera with unidentified morphology in thin section. The test chambers are cemented with calcite. Plane polarized light. Photomicrographs A (20x magnification), B (20x magnification), C (20x magnification), D (20x magnification) and E (20x magnification) correspond to upper Eagle Ford, sample #GZ-4, Well #1; photomicrograph F (20x magnification) corresponds to upper Eagle Ford, sample #GZ-6, Well #1.
Figure 4.7b Photomicrographs of foraminifera with unidentified morphology in thin section. The test chambers are cemented with calcite in A and E, and a mixture of clays and organic matter in B, C, D and E. Plane polarized light. Photomicrograph A (20x magnification) corresponds to upper Eagle Ford, sample #GZ-5, Well #1; photomicrograph B (40x magnification) corresponds to upper Eagle Ford, sample #GZ-6, Well #1; photomicrograph C (20x magnification) corresponds to upper Eagle Ford, sample #GZ-7, Well #1; photomicrograph D (40x magnification) corresponds to lower Eagle Ford, sample #LS-1, Well #2; photomicrograph E (40x magnification) corresponds to lower Eagle Ford, sample #LS-5, Well #2.
4.2 Echinoderms

The echinoderms are benthonic marine invertebrates that can be found in shallow-marine and deep-marine environments. The skeleton is internally composed of a series of calcareous plates. After death, the skeletons disarticulate and the plates and spines are deposited on the sea floor. The plates range in size from millimeters to centimeters. They are polygonal-shaped and show undulatory extinction between crossed nicols (Flügel, 2004) (Figure 4.8).

4.3 Bivalves

The bivalves are benthic organisms composed of two layered shell valves. They can be found in all aqueous environments, from hypersaline to fresh water. The length of these organisms ranges from less than 1 mm to approximately 2 m, as it is the case of inoceramids (Scholle and Ulmer-Scholle, 2006). Fragments of these organisms are not abundant in the available thin sections. One example is shown in Figure 4.10, where inoceramid and oyster fragments are recognized.

4.4 Fish bones

Fish bones are phosphatic bioclasts easily recognizable in thin sections. Under plane light, they present brown-to pale yellow colors. Under cross polarized light, they are always dark. Fish bones of different sizes and skeletal parts are recognized in the available thin sections from different samples (Figure 4.11).

4.5 Radiolaria

The radiolaria are marine planktonic protozoans. They can be found at all depths but are more abundant in deep-sea sediments. The composition of radiolaria tests is siliceous, more
specifically amorphous opaline silica. The size of these microfossils ranges from less than 100 µm to over 2 mm (Scholle and Ulmer-Scholle, 2006) (Figure 4.12).

Figure 4.8 Photomicrographs of echinoderm plates and spines. (A) Echinoderm plates under plane polarized light. 20x magnification. (B) Same photomicrograph under cross polarized light. Upper Eagle Ford, sample #GZ-4, Well #1. (C) Echinoderm plates under plane polarized light. 10x magnification. (D) Same photomicrograph under cross polarized light. Upper Eagle Ford, sample #GZ-8, Well #1.
Figure 4.9 Continued  (E) Transversal section of echinoderm spine under plane polarized light. 40x magnification. (F) Same photomicrograph under cross polarized light. Lower Eagle Ford, sample #LS-5, Well #2. (G) Equatorial section of echinoderm spine under plane polarized light. 20x magnification. (E) Same photomicrograph under cross polarized light. Lower Eagle Ford, sample #LS-5, Well #2.
4.6 Coccoliths

The coccoliths are calcareous (low-magnesium calcite) exoskeletal plates produced by coccolithophores, a type of planktonic unicellular algae. These organisms live in surface waters but can be deposited in deep marine environments above the calcite compensation depth (CCD) (Scholle and Ulmer-Scholle, 2006). A cccosphere presents a diameter between 2 and 25 µm that is composed of 10 to 150 coccoliths on its surface. Each coccolith has an approximate diameter of 1-15 µm (Kennet, 1982; Scholle and Ulmer-Scholle, 2006). The micrometric size of these fossils makes very difficult their recognition at thin section. Therefore, SEM is the most common technique used to identify them in rock samples. Figure 4.13a and figure Figure 4.12b show coccoliths impressions found in the upper Eagle Ford. Coccoliths are also present in fecal pellets as shown in Figure 4.13a and Figure 4.13b in the lower Eagle Ford.

4.7 Calcispheres

The calcispheres are spherical microfossils with thick walls composed of calcite. These microfossils are interpreted as algal remains although for a long time they have been considered a microproblematica in terms of systematic position. Calcispheres from the Cretaceous are considered to be calcareous dinoflagellate algae (Flügel, 2004) (Figure 4.14).
Figure 4.10 Photomicrographs of bivalves. (A) Inoceramid fragment (black arrow) and oyster fragments (white arrows). Also, note the well-rounded phosphate nodule in the middle of the photomicrograph. Plane polarized light. 2.5x magnification. (B) Inoceramid fragment showing drusy calcite composition under cross polarized light. Oyster fragments are characterized by showing undulatory extinction under cross polarized light. Lower Eagle Ford, sample LS-4, Well #2.
Figure 4.11 Photomicrographs of fish bones. (A) Fish vertebra where the intraparticle pore space is filled with micrite. Plane polarized light. 10x magnification. Upper Eagle Ford, sample #GZ-8, Well #1. (B) Fish scale of less than 1 mm long. Plane polarized light. 10x magnification. Upper Eagle Ford, sample #GZ-4, Well #1. (C) Jaw fragment (white arrow). Plane polarized light. 20x magnification. Upper Eagle Ford, sample #GZ-8, Well #1. (D) ‘Saw’ shaped jaw fragment. Plane polarized light. 40x magnification. Upper Eagle Ford, sample #GZ-8, Well #1. (E) Fish scale of more than 1 mm long. Plane polarized light. 10x magnification. Upper Eagle Ford, sample #GZ-8, Well #1.
Figure 4.12 Photomicrographs of radiolaria. (A) Partially recrystallized radiolaria under plane polarized light. 10x magnification. (B) Same photomicrograph under cross polarized light. Upper Eagle Ford, sample #GZ-7', Well #1. (C) Cortical radiolaria shell under plane polarized light. 40x magnification. (D) Same photomicrograph under cross polarized light. Note the pores on the shell surface. Upper Eagle Ford, sample #GZ-4, Well #1. (E) Radiolaria under plane polarized light. 40x magnification. Note the moderately preserved spines (black arrow). (F) Same photomicrograph under red light. Upper Eagle Ford, sample #GZ-8, Well #1.
Figure 4.13a  SEM image of coccolith impressions. 6,500x magnification. Upper Eagle Ford, sample #GZ-7, Well #1.

Figure 4.12b  SEM image of coccolith impressions. 10,000x magnification. Upper Eagle Ford, sample #GZ-7, Well #1.
Figure 4.13a  BSE SEM image of fecal pellet (highlighted in yellow). 1,600x magnification. Lower Eagle Ford, sample #GZ-9, Well #1.

Figure 4.13b  Close-up BSE SEM image of Figure 4.13a showing coccoliths within the fecal pellet (white arrows). 13,000x magnification.
Figure 4.14 SEM image of calcisphere. Upper Eagle Ford, sample #GZ-7, Well #1.
CHAPTER 5

PORE SYSTEM CHARACTERIZATION

The aim of this chapter is to provide a pore system characterization of the Eagle Ford Shale in Gonzales and La Salle counties. A porosity quantitative study coupled with SEM imaging study of core samples helped to better understand the pore system of the Eagle Ford Shale. Different hypothesis can be formulated to explain the reason behind the large oil production numbers in the Eagle Ford, such as: 1) the pore system plays a significant role in creating a flowing network that helps to deliver large amounts of hydrocarbons; 2) the abundance of natural microfractures that create preferential pathways for the hydrocarbons to flow might be larger than previously thought; and 3) a combination of the two previously mentioned hypotheses. Therefore, a pore system characterization is necessary to understand where the hydrocarbons may be stored and how they flow through the pore network.

5.1 Quantitative analysis of porosity

A quantitative study of the available core samples was conducted based on two different methods: water immersion porosimetry (WIP); and 2) mercury injection capillary pressure (MICP). The total porosity results obtained from these methods are indicative of the potential oil/gas storage of the rock, while pore structure will potentially affect the gas/oil recovery rate (Gao and Hu, 2012).

5.1.1 Water immersion porosimetry (WIP)

In order to measure total porosity of the available rock samples, the WIP method has been performed. This method, developed by Kuila (2013), represents an alternative to the existing Gas Research Institute (GRI) method where preparation of samples involves crushing the rock and an aggressive pretreatment. The total porosity obtained from WIP corresponds to
the total water accessible porosity, where the water adsorbed on clay surfaces is also included (Kuila et al., 2013). The steps followed to perform this experiment are as follows:

- Step 1: five rock samples per core interval were cut by using a dry-cut saw. The total weight of all five samples together ranges between 1.75-6.24 g. Once cut, the samples were cleaned with an air pressure gun to remove any residual particles that might be present on their surface. The samples were then degassed in vacuum at 200°C during 24 h to remove any fluids that might exist in the rock. Once the vacuum was completed, the dry weight ($\text{DryWt}_{\text{air}}$) was measured by using a moisture analyzer (Mettler Toledo HB43™).

- Step 2: after weighting, the samples were put under vacuum (20.5 in Hg) for three days.

- Step 3: 3 % KCl deionized water was injected for saturation of the samples. The samples were under saturation conditions for seven days. The reason for using 3 % KCl deionized water was to avoid the expansive effect that might have occurred if expandable clay minerals were present in the rock.

- Step 4: the saturated samples were weighted five times both in air ($\text{SatWt}_{\text{Air}}$) and submerged in 3 % KCl deionized water ($\text{SatWt}_{\text{Sub}}$) by using a Jolly Balance (Mettler Toledo XS™).

In order to calculate the total porosity, the bulk density must be calculated first:

$$\rho_B = \left( \frac{\text{SatWt}_{\text{Air}}}{\text{SatWt}_{\text{Air}} - \text{SatWt}_{\text{Sub}}} \times (\rho_{\text{H}_2\text{O}} - \rho_{\text{air}}) \right) + \rho_{\text{air}}$$

where

$\rho_B$ = bulk density (g/cm$^3$)

$\rho_{\text{H}_2\text{O}} = 1.018525$ g/cm$^3$ - density of 3 % KCl deionized water

$\rho_{\text{air}} = 0.0012$ g/cm$^3$ – air density
Then, the anhydrous grain density is calculated:

\[
\rho_G = \left[ \frac{\text{Dry} Wt_{Air}}{\text{Dry} Wt_{Air} - \text{Sat} Wt_{Sub}} \times (\rho_{H_2O} - \rho_{air}) \right] + \rho_{air}, \text{ where}
\]

\[
\rho_G = \text{anhydrous grain density (g/cm}^3\text{)}
\]

Finally, the total porosity is calculated:

\[
\phi_{WIP} = \frac{(\rho_B - \rho_G)}{(\rho_{H_2O} - \rho_G)} \times 100, \text{ where}
\]

\[
\phi_{WIP} = \text{total porosity (%)}
\]

The results obtained from WIP are shown in Figure 5.1. The lower Eagle Ford at Well #1 location shows a sharp increase in porosity compared to the upper Eagle Ford at the same well and the lower Eagle Ford at Well #2 location. One of the reasons for this difference in total porosity values might be the difference in mineralogical composition between rock samples. Total porosity increases with increasing clay content as shown in Figure 5.2. This indicates that a large part of the water has potentially been adsorbed on clay surfaces for those samples with larger clay content (lower Eagle Ford, Well #1). In contrast, Figure 5.3 indicates a decrease in porosity with increase in total carbonate content.

### 5.1.2 Mercury injection capillary pressure (MICP)

MICP is an analysis that measures the pore throat size in rock samples. Mercury is a non-wetting fluid that will not intrude the pores by capillary action. Thus, an external force or pressure must be applied on the fluid so it can intrude into the pore space. The smaller the pore throat the larger the pressure that must be applied on the mercury to intrude the pore space. The experiment is performed by progressively increasing the pressure applied on the mercury. Pressure versus intrusion data are collected during the experiment. These data permit the MICP machine to automatically compute volume and pore-throat size distributions.
Figure 5.1  Water immersion porosimetry results.
Figure 5.2  Scatter-plot of calculated total porosity in WIP and measured total clays content in XRD.

Figure 5.3  Scatter-plot of calculated total porosity in WIP and measured total carbonates content in XRD.
According to the pore-size classification proposed by Loucks et al., 2012, those pores between 1 nm and less than 1 µm are considered nanopores, pores between 1 µm and less than 62.5 µm are considered micropores, and mesopores correspond to pores between 62.5 µm and less than 4 mm. This classification has been used as a reference for the pore throat diameter calculations obtained from the experiment.

Pore throat diameter histograms were generated to better visualize and understand the pore throat size distribution for each sample. The upper portion of the upper Eagle Ford member (i.e., samples #GZ-4, #GZ-5 and #GZ-6) presents a pore throat size distribution restricted to the nanopore-size range. In contrast, the lower portion (i.e., samples #GZ-7 and #GZ-8) presents a broader spectrum of pore throat diameters, covering the nanopore, micropore and mesopore ranges, where nanopores represent the most frequent pore throat size (Figure 5.4). The lower Eagle Ford member in the same well is dominated by nanopore and micropore throat sizes. Mesopore throat sizes are also present in sample #GZ-9 (Figure 5.5).

The lower Eagle Ford member in Well #2 shows a pore throat size histogram similar to the same member in Well #1 (Figure 5.6). The only exceptions are samples #LS-3 and #LS-5 where the pore throat size distribution is similar to that in the upper portion of the upper Eagle Ford. Figure 5.7 shows the cumulative pore throat size histogram where all the samples that correspond to the same member are considered and plotted together. The upper and lower Eagle Ford at both well locations present pore throat diameters within the nanopore, micropore and mesopore size ranges. However, the upper Eagle ford is dominated by pore throat diameters within the nanopore size range, while the lower Eagle Ford at both well locations is dominated by pore throat diameters within both the nanopore and micropore size ranges.
Figure 5.4  Pore throat size histograms for the upper Eagle Ford, Well #1.
MICP also measures the total porosity of the analyzed rock samples. The results show that the lower Eagle Ford at Well #2 is the most porous member, with a total porosity ranging between 3.34-10.27 %. The lower Eagle Ford and lower portion of the upper Eagle Ford show a total porosity between 3.73-4.63 per cent. In contrast, the total porosity of the upper portion of the upper Eagle Ford is between 0.32-1.41 per cent (Figure 5.8).

The total porosity values obtained from MICP differ from those obtained from WIP. When correlating the total porosity values obtained from each method, it can be clearly seen that the correlation is very poor (Figure 5.9). One of the reasons might be the different behavior that the rock components experience when they are in contact with the fluid used for each experiment (i.e., mercury and 3 % KCl deionized water). Clays absorbed water with a subsequent increase in weight after saturating the samples. This increase in weight, which does not correspond to water inside the pores, might have biased the total porosity results obtained from WIP.
Figure 5.6. Pore throat size histograms for the lower Eagle Ford, Well #2.
Figure 5.7 Cumulative pore throat diameter histogram.
Figure 5.8 MICP total porosity results.
Figure 5.9  Correlation between porosities obtained from MICP and WIP.

Figure 5.10 shows the calculated MICP permeability versus total porosity for the analyzed core samples. It can be seen that there is a direct correlation between total porosity and permeability of the rock. The highest permeability values correspond to the lower Eagle Ford at Well #2 location (0.03737-0.86467 µd) while the lowest correspond to the upper portion of the upper Eagle Ford at Well #1 (0.0260-0.02647 µd). The lower portion of the Eagle Ford shows calculated permeability values between 0.05219-0.10078 µd. Among other factors, for the permeability to increase, the porosity needs to be effective porosity. In those samples where the permeability is higher, the most common porosity observed on SEM is intraparticle organic matter porosity. This suggests that the organic matter porosity creates a 3D pore network that contributes to an increase in the permeability. The calculation of permeability from MICP results is based on the correlation between permeability and mercury capillary pressure proposed by Swanson (1981). Nevertheless, this permeability should be considered only as a first
screening process for evaluating the potential permeability values for rocks analyzed with MICP experiment. Its accuracy is questionable for tight rocks such as organic rich mudrocks and obtained results should be contrasted with permeability values acquired from different experiments (e.g., pulse decay permeametry).

Figure 5.10  MICP porosity vs MICP permeability.

5.2  Imaging study of pore types

A better understanding of mudrocks at microstructure scale, including the pore type and geometry, can help to better understand production rates and reserves (Loucks et al., 2010). For this purpose, a qualitative study of the existent pore types in the available Eagle Ford Shale core
samples has been performed by using SEM. Ar-ion milled rock samples were used to ensure that the pores identified are ‘in-situ’. The pore type classification and nomenclature proposed by Loucks et al. (2012) (Figure 5.11) has been followed as a reference for this research study. In this classification, matrix-related pores in mudrocks can be categorized based on their relationship with adjacent particles as: 1) interparticle (interP) pores; 2) intraparticle (intraP) pores; and intraparticle organic matter (OM) pores. Fracture pores are not controlled by mineral matrix and therefore they do not belong to any of the aforementioned classification categories (Loucks et al., 2012). Note that dual pore systems consist of a combination of fracture pores and matrix-related pore networks (Loucks et al., 2010).

5.2.1 Interparticle pores

Interparticle pores correspond to void spaces that are present between crystals and grains. At the time of deposition, the unconsolidated mudrock contains larger percentage of interparticle pores. Due to the soft and ductile character of some components that might be present in the rock, diagenetic processes (e.g., compaction, cementation) decrease interparticle effective porosity throughout burial. As a result, the former interparticle pore network is destroyed to some extent. Hence, interparticle pore geometries will vary depending on the primary pore preservation and diagenetic alteration of the rock (Loucks et al., 2010; Loucks et al., 2012). Examples of interparticle pores found in the available rock samples are shown in Figure 5.12.

5.2.2 Intraparticle pores

Intraparticle pores correspond to void spaces occurring within particles. Most of these pores are diagenetic, although some of them might be primary in origin. There seems to be a correlation between abundance of intraparticle pores and age. In general, intraparticle pores are more abundant in younger mudrocks than in older mudrocks. Intraparticle pore types examples
are: 1) intercrystalline pores within pyrite framboids; 2) intraplatelet pores within clay aggregates (i.e., cleavage-plane pores); 3) pores within peloids of pellets (i.e., intragrain pores); 4) dissolution-rim pores; 5) pores within fossil bodies (i.e., intrafossil pores); and 6) moldic pores after partial or complete dissolution of a crystal or fossil (Loucks et al., 2010; Loucks et al., 2012). Examples of intraparticle pores found in the available rock samples are shown in Figure 5.13 and Figure 5.14.

Figure 5.11  Pore type classification in mudrocks. Adapted from Loucks et al. (2012).
Figure 5.12 SEM photomicrographs of interparticle pores. Ar-ion milled sample. (A) Yellow arrows indicate nanometer-size interparticle pores between crystals; red arrows indicate nanometer-size interparticle pores at the edge of rigid grains; and blue arrow indicates nanometer-size interparticle pore between clay platelets. 10,000x magnification. Lower Eagle Ford, sample #LS-5, Well #2. (B) Image of micrometer-size interparticle pore between calcite crystals. 27,000x magnification. Lower Eagle Ford, sample #LS-5, Well #2.
Figure 5.13  SEM photomicrographs of intraparticle pores. Ar-ion milled samples. (A) Yellow arrows indicate nanometer-size pores within rhabdoliths; red arrow indicates nanometer-size moldic pore after a crystal. 7,500x magnification. Upper Eagle Ford, sample #GZ-4, Well #1. (B) Image of calcite crystal with nanometer-size fluid-inclusions (?) intraparticle pores (yellow arrows). 3,500x magnification. Upper Eagle Ford, sample #GZ-8, Well #1.
Figure 5.14  SEM photomicrographs of intraparticle pores. Ar-ion milled samples (A) Nanometer-size intraparticle pores within pyrite framboid (yellow arrows). 6,500x magnification. Upper Eagle Ford, sample #GZ-4, Well #1. (B) Close-up image of cleavage-sheet intraplatelet pores within clays. 11,000x magnification. Lower Eagle Ford, sample #LS-3, Well #2.
5.2.3 Intraparticle organic matter pores

Intraparticle organic matter pores correspond to those void spaces occurring within the organic matter. The geometry and distribution of this type of pores will depend on the thermal maturation history and subsequent potential hydrocarbon generation of the organic matter. The qualitative categorization of organic matter pores proposed by Milliken et al. (2013) (Figure 5.15) has been followed in this study to classify this porosity type. In conjunction with the abovementioned pore categorization, the classification of organic matter texture proposed by Dahl et al. (2012) has been used to complement this imaging study (Figure 5.16). The organic matter type (i.e., detrital and secondary organic matter) found in the Eagle Ford Shale samples is further studied and discussed in Chapter 6 of this research work.

Most organic matter pores types and textures have been found in the analyzed core samples in the upper Eagle Ford (Figure 5.17, Figure 5.18 and Figure 5.19) and lower Eagle Ford (Figure 5.19) at Well #1 location, and lower Eagle Ford at Well #2 location (Figure 5.20, Figure 5.21, and Figure 5.22). Based on the SEM images analyzed from both wells, the organic matter texture in the lower Eagle Ford at Well #2 location is predominantly spongy-type. The reason behind that is most likely due to the higher degree of thermal maturation and subsequent natural gas generation and expulsion from the organic matter (e.g., bitumen) that occurred in the lower Eagle Ford at Well #2.
Figure 5.17 SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples (A) Mineral-associated organic matter porosity primarily of micrometer-size. The organic matter shows fracture-type texture. 3,500x magnification. Upper Eagle Ford, sample #GZ-5, Well #1. (B) Mineral-associated organic matter porosity in the nanometer-to-micrometer size range. The organic matter shows fracture-to-pendular-type texture. 8,000x magnification. Upper Eagle Ford, sample #GZ-6, Well #1.
Figure 5.18 SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples (A) Discrete spongelike organic matter porosity, primarily of micrometer-size. The organic matter shows pendular-to-fracture-type texture. Yellow box indicates area of image B. 15,000x magnification. (B) Higher-magnification view of the image area indicated in (A). Note the complex 3D structure and different pore throat geometries. 40,000x magnification. Upper Eagle Ford, Sample #GZ-6, Well #1.
Figure 5.19 SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples (A) Complex organic matter porosity ranging from nanometer-to-micrometer-size. Yellow arrows indicate some of the pores found in this sample. The organic matter shows pendular-to-fracture-type texture. 30,000x magnification. Upper Eagle Ford, sample #GZ-5, Well #1. (B) Discrete, isolated organic matter porosity (yellow arrows). 5,000x magnification. Lower Eagle Ford, sample #LS-5, Well #2.
Figure 5.20  SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples (A) Complex organic matter porosity with bimodal distribution of pore sizes inside foraminifera test chamber. The organic matter primarily shows pendular-type texture. Yellow box indicates area of image B. 2,000x magnification. (B) Higher-magnification view of the image area indicated in (A). The bimodal distribution of pore sizes is clearly seen in this image. Yellow arrow indicates pores within the micrometer-to-nanometer-size range. Red arrow indicates pores within the nanometer-to-picometer-size range. 30,000x magnification. Lower Eagle Ford, sample #LS-1, Well #2.
Figure 5.21 SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples. (A) Complex organic matter porosity. The organic matter is located in the former intercrystalline pore space and shows pendular-to-spongy-type texture. 13,000x magnification. Lower Eagle Ford, sample #LS-4, Well #2. (B) Discrete spongeliike organic matter porosity. The organic matter is distributed in the former intercrystalline pore space and has spongy-type texture. Pores tend to form aligned clusters in some parts of the organic matter (yellow arrows). 20,000x magnification. Lower Eagle Ford, sample #LS-5, Well #2.
Figure 5.22 SEM photomicrographs of intraparticle organic matter pores. Ar-ion milled samples (A) 3D spongy network of complex organic matter porosity. The organic matter is located in the former intercrystalline pore space and shows spongy-type texture. 5,000x magnification. (B) BSE image of (A). Lower Eagle Ford, sample #LS-2, Well #2.
5.2.4 Microfractures

Identification of natural microfractures on SEM and transmitted light microscopy is very difficult. Most microfractures observed on samples using SEM are induced as a result of shrinkage during core and/or samples manipulation and preparation (Figure 5.23). Nonetheless, healed microfractures, also referred to as calcite veins (Flügel, 2004), were observed on thin section and SEM in some of the samples analyzed. These microfractures are not abundant but might have contributed to the hydrocarbon migration flow-network before they healed.

Figure 5.23 Shrinkage microfractures observed on SEM (yellow arrows). Ar-ion milled samples. (A) 10,000x magnification, upper Eagle Ford, sample #GZ-7, Well #1. (B) 5,000x magnification, and (C) 7,000x magnification, correspond to upper Eagle Ford, sample #GZ-8, Well #1. (D) 7,000x magnification, lower Eagle Ford, samples GZ-10, Well #1.
Two types of calcite veins were found in the Eagle Ford rock samples: Type I and Type II (Figure 5.24). Type I microfractures (Figure 5.25) are composed of sparry calcite and do not cross any microfossil or mineral grains. These microfractures do not show straight edges and the boundary microfracture-matrix is diffuse at some parts. In general, their orientation is perpendicular-to-oblique to the bedding plane. They are not uniform in terms of length and thickness. Within the same microfracture, the thickness ranges between 10-250 µm. Lengths range between 1.5-9 mm. This type of microfracture is most likely formed during early diagenesis as a result of dewatering of the sediments. (Flügel, 2004). Compaction is also evident from the wavy nature observed in Figure 5.25. Type II microfractures are composed of calcite and cross several microfossils (Figure 5.26). The orientation is predominantly perpendicular to the bedding plane. The thickness (30 µm) does not vary along the fracture and the length is over 20 mm. This microfracture was formed during post-diagenetic processes, when the mudrock was well-consolidated.
Figure 5.24 (A) Photomicrograph of Type I and Type II microfractures. Yellow box indicates enlarged area of B and C. The scale bar is 1 mm. Plane polarized light. 2.5x magnification. (B) Enlarged view of A. Note the differences in the microfracture-matrix boundary between both microfracture types. Plane polarized light. 10x magnification. (C) Same photomicrograph under cross polarized light. Upper Eagle Ford, sample #GZ-4, Well #1.
Figure 5.25 Photomicrographs of Type I microfractures. (A) Broad view of healed microfractures. Note the variation in thickness. The scale bar is 1 mm. Yellow box indicates enlarged area in B. Red box indicates enlarged area in C and D. Plane polarized light. 2.5x magnification. (B) Close-up image of A. Cross polarized light. 2.5x magnification. (C) Higher-magnification view of the red box area indicated in A. Plane polarized light. 10x magnification. (D) Same photomicrograph under cross polarized light. Note the texture of the sparry calcite filling the pore space within the fracture. Upper Eagle Ford, sample #GZ-5, Well #1.
Figure 5.26 (A) Photomicrographs of Type I and Type II microfractures. Red box indicates enlarged area of B and C. The scale bar is 1 mm. Plane polarized light. 2.5x magnification. (B) Enlarged view of A, showing the microfracture Type I crossing an echinoderm plate. Plane polarized light. 10x magnification. (C) Same photomicrograph under cross polarized light. Upper Eagle Ford, sample #GZ-4, Well #1.
CHAPTER 6

ORGANIC MATTER CHARACTERIZATION AND HYDROCARBON POTENTIAL

The objective of this chapter is to evaluate the hydrocarbon potential of the analyzed core intervals in Well #1 and Well #2. For this purpose, the available core samples were analyzed by using two different Rock-Eval methods: 1) the Basic/Bulk-Rock method; and 2) the IFPEN Shale Play method. The results obtained from Rock-Eval analysis helped to better identify the most potential intervals in terms of oil-in-place (OIP). This assessment has been coupled with SEM imaging study to better understand the organic matter type and distribution in the rock samples depending on the amount of hydrocarbon content.

6.1 Self-contained source-reservoir system

The potential to contain and/or generate hydrocarbons of every source and reservoir rock is evaluated based on geochemical analyses. Pyrolysis is the most widely accepted geochemical analysis used in the oil and gas industry. It provides the necessary information to evaluate the type of kerogen and maturity, total organic carbon, and in situ petroleum shows (Romero-Sarmiento et al., 2015). Pyrolysis analysis basically consists in heating the organic matter contained in a rock sample under anoxic conditions, in an inert atmosphere (helium or nitrogen). Free organic compounds (i.e. bitumen) are distilled first, followed by a cracking of pyrolytic products from insoluble organic matter (i.e. kerogen) as oven temperature increases. Any organic compounds expelled during the analysis are recorded by a flame ionization detector (FID). The results are automatically plotted in a pyrogram where three peaks are recognized: 1) the $S_1$ peak that corresponds to the available free hydrocarbons that are susceptible of being volatilized, measured in mg HC/g rock; 2) the $S_2$ peak that shows the potential of a source rock to generate petroleum, measured in mg HC/g rock. This peak corresponds to the amount of hydrocarbons.
yielded from cracking of kerogen; and 3) the S₃ peak that measures the carbon dioxide content in mg CO₂/g rock. This analysis also records the T_max that corresponds to the temperature at maximum S₂ peak. Likewise, the analysis measures the hydrogen index (HI) and oxygen index (OI). The HI is an indicative value of the potential of a given rock sample to generate oil based on the amount of hydrogen present in the kerogen. It is measured in mg HC/g TOC. OI corresponds to the amount of oxygen in the kerogen, measured in mg CO₂/g TOC. Pyrolysis analysis also measures the amount of organic carbon (i.e. TOC), including both kerogen and bitumen, present in the rock samples. This parameter is measured in wt. % (Peters, 1986; Peters and Cassa, 1994; Behar et al., 2001).

In this research, the available Eagle Ford Shale samples have been analyzed using the new IFPEN Shale Play method, developed by the IFP Energies Nouvelles (France). Existing methods (e.g. Rock-Eval Basic/Bulk-Rock) consider the shale rock as the source rock only. The new IFPEN method helps to better evaluate the potential of an organic rich shale rock because it considers the rock as both the source and reservoir rock. It presents an improvement in the quantification of free or sorbed hydrocarbons in shale rocks. Also, it provides a more accurate measurement of the T_max parameter (Romero-Sarmiento et al., 2015).

The main difference between the new Shale Play Method and other existing Rock-Eval methods is the programmed ramp of temperature during pyrolysis (Figure 6.1). The ‘classic’ Rock-Eval method starts the pyrolysis at a temperature of 300°C, which is assumed to be the temperature of thermal cracking of kerogen. The ‘reservoir’ Rock-Eval method provides a good estimation of low-molecular weight hydrocarbons by starting pyrolysis at 180°C (Romero-Sarmiento et al., 2015). According to the procedure described by Romero-Sarmiento et al. (2015), the new IFPEN Shale Play Method starts the pyrolysis at a temperature T₁ of 100°C,
where thermovaporization of hydrocarbons initiates. At this stage, the lightest hydrocarbons that might be present in the rock are captured and quantified. The temperature is then increased up to a temperature equal to 200°C (T₂) at a rate of 25°C/min. This temperature is then maintained constant during three minutes. Thermovaporizable hydrocarbons are released and quantified during this stage. During the third stage, the temperature is increased at the same rate as the previous stage (25°C/min) up to a temperature equal to 350°C (T₃), which is then maintained constant during three minutes. The thermovaporized heavy molecular weight compounds are quantified during this stage. In the final stage, the temperature is increased again at a rate of 25°C/min up to a temperature equal to 650°C (T₄). During this stage, the pyrolyzable part of the remaining organic matter is released and quantified. A more detailed description of the new Rock-Eval method can be found in Romero-Sarmiento et al. (2015).

Compared to existing Rock-Eval methods, the IFPEN Shale Play Method provides pyrograms containing three key parameters: Sh0, Sh1 and Sh2 (Figure 6.2). The Sh0 peak

Figure 6.1 Ramp of temperature settings for the Basic/Bulk-Rock, Shale Play and Reservoir methods. From Romero-Sarmiento et al. (2015).
corresponds to the amount of the lightest thermovaporized hydrocarbons that are released between 100°C \( (T_1) \) and 200°C \( (T_2) \), measured in mg HC/g rock. The Sh1 peak indicates the amount of heavier thermovaporized hydrocarbons that are released between 200°C \( (T_2) \) and 350°C \( (T_3) \). The amount of released thermovaporized high-molecular weight hydrocarbons along with hydrocarbons yielded from the pyrolysis of organic matter is illustrated by the Sh2 peak. The corresponding temperature interval for the Sh2 peak is 350°C \( (T_3) \) and 650°C \( (T_4) \).

![Pyrogram type obtained from the IFPEN Shale Play method, Bazhenov Shale sample.](image)

Figure 6.2  Pyrogram type obtained from the IFPEN Shale Play method, Bazhenov Shale sample. The addition of both Sh0 and Sh1 peaks obtained from the IFPEN Shale Play method is equivalent to the S_1 peak obtained from the Basic/Bulk Rock-Eval method. From Romero-Sarmiento et al. (2015).

The available Eagle Ford rock samples were sent to IFPEN in France to be analyzed by using the IFPEN Shale Play method. The samples were also analyzed by using the Basic/Bulk-Rock method to compare results between both methods. In order to determine the kerogen type, the results obtained from the analysis (Romero-Sarmiento et al., 2016) are plotted in a modified van Krevelen diagram (Figure 6.3). In this diagram, the x-axis and y-axis correspond to the OI and HI respectively. In general, higher hydrogen content corresponds to higher oil-generative potential and lower thermal maturity (Peters and Cassa, 1994). The results were also plotted in
the Espitalie diagram (Espitalie et al, 1977), where the x-axis and y-axis correspond to the $T_{\text{max}}$ and HI respectively (Figure 6.4). The modified van Krevelen diagram shows that the samples analyzed for the Eagle Ford Shale are marine oil-prone type II source rocks, located in the mature, oil window. Lower Eagle Ford samples from Well #2 show lower HI and similar-to-lower OI values compared to lower and upper Eagle Ford samples from Well #1. The lower HI values in these samples are the consequence of oil and gas generation from the original kerogen. Oil and gas are rich in hydrogen. As these products are generated due to thermal maturation, the kerogen becomes depleted in hydrogen (Peters and Cassa, 1994). The Espitalie diagram shows that lower Eagle Ford samples from Well #2 and part of the upper Eagle Ford samples from Well #1 plot in the oil-gas prone kerogen type. This indicates that gas generation might have also occurred during thermal maturation from these source rock samples.

As previously mentioned, Sh0 and Sh1 parameters are representative of the amount of hydrocarbons that are present in the analyzed rock samples. Figure 6.5 shows the recovery in milligram of hydrocarbons per gram of initial rock based on the results obtained from the analysis. Both the Basic/Bulk-Rock and Shale Play methods are included for a better comparison between the results obtained from each of them.

The difference in the quantification of hydrocarbons per rock sample between both methods ranges between 17.41-40.63 %, with an average of 25.69 % (Table 6.1). Based on these numbers, the new Shale Play method can better identify potential targets when evaluating the hydrocarbons content potential (e.g. OIP) of different intervals within the same well. An increase of 25 % in hydrocarbons content will definitely influence in the economic evaluation of a well.
Figure 6.3  Modified van Krevelen diagram. Rock samples from both wells fall within the same kerogen type category.
Figure 6.4 Espitalie diagram. Rock samples from both wells are located in the oil window. Note that in this diagram the rock samples from the lower Eagle Ford, Well #2 and some of the upper Eagle Ford, Well #1 plot within the type II-III oil-gas-prone kerogen. This indicates that the kerogen present in these samples is more mature compared to those samples plotting within the Type II kerogen.
Figure 6.5  Comparison of $S_1$ and $Sh0 + Sh1$ parameters from Basic/Bulk-Rock and Shale Play methods respectively.
Table 6.1  Calculated percentage increase in hydrocarbons quantification between Basic/Bulk-Rock method and Shale Play method.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>S1 from Basic/Bulk-Rock method (mg HC/ g rock)</th>
<th>Sh0+Sh1 from Shale Play method (mg HC/ g rock)</th>
<th>Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>3.15</td>
<td>4.42</td>
<td>28.65</td>
</tr>
<tr>
<td>GZ-5</td>
<td>1.84</td>
<td>2.30</td>
<td>20.04</td>
</tr>
<tr>
<td>GZ-6</td>
<td>2.71</td>
<td>3.55</td>
<td>23.55</td>
</tr>
<tr>
<td>GZ-7</td>
<td>6.00</td>
<td>8.22</td>
<td>26.96</td>
</tr>
<tr>
<td>GZ-8</td>
<td>5.00</td>
<td>6.74</td>
<td>25.84</td>
</tr>
<tr>
<td>GZ-9</td>
<td>1.41</td>
<td>2.38</td>
<td>40.63</td>
</tr>
<tr>
<td>GZ-10</td>
<td>1.84</td>
<td>2.67</td>
<td>30.96</td>
</tr>
<tr>
<td>LS-1</td>
<td>16.98</td>
<td>20.56</td>
<td>17.41</td>
</tr>
<tr>
<td>LS-2</td>
<td>18.55</td>
<td>22.69</td>
<td>18.27</td>
</tr>
<tr>
<td>LS-3</td>
<td>9.30</td>
<td>12.59</td>
<td>26.17</td>
</tr>
<tr>
<td>LS-4</td>
<td>9.35</td>
<td>12.45</td>
<td>24.91</td>
</tr>
<tr>
<td>LS-5</td>
<td>5.02</td>
<td>6.68</td>
<td>24.85</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>25.69</strong></td>
<td><strong>5.68</strong></td>
<td></td>
</tr>
</tbody>
</table>

Based on the results obtained from the Shale Play method, the most prospective intervals are those corresponding to Well #2, samples #LS-1 (20.56 mg HC/g rock), #LS-2 (22.69 mg HC/g rock), #LS-3 (12.59 mg HC/g rock) and #LS-4 (12.45 mg HC/g rock), and potentially #LS-5 (6.68 mg HC/g rock), all of them corresponding to the lower Eagle Ford member. In contrast, the lower Eagle Ford at Well #1 location does not show great potential in terms of hydrocarbons content. At Well #1 location, the lower portion of the upper Eagle Ford member has greater potential based on results obtained for samples #GZ-7 (8.22 mg HC/g rock), and potentially #GZ-8 (6.74 mg HC/g rock).

Downey et al. (2011) proposed a quick-look approach to quantitatively measure the oil-in-place based on $S_1$ values obtained from Rock-Eval pyrolysis. In this research, a modified approach adapted to the IFPEN Shale Play method, where Sh0 and Sh1 values are considered, is proposed as follows:
- Step 1: calculation of grams of oil per section

\[ M_{Sh0+Sh1HC} = \frac{(Ah\rho_{AV}(Sh0+Sh1)_{AV}) \times 0.001}{8.11E-10}, \text{ where} \]

- Mass of Sh0 + Sh1 hydrocarbons per section (g)
- \( A = \) Area of interest in acres (sectional area – 640 acres)
- \( h = \) Reservoir height (ft)
- \( \rho_{AV} = \) Average bulk density (g/cm^3)
- \( (Sh0 + Sh1)_{AV} = \) Average Sh0 + Sh1 (mg/g)

- Step 2: calculation of volume of oil per section

\[ V_{Sh0+Sh1HC} = \left( \frac{M_{Sh0+Sh1HC}}{\rho_{oil}} \right) \times 159, \text{ where} \]

- Volume of Sh0+Sh1 hydrocarbons per section (bbl)
- Mass of Sh0 + Sh1 hydrocarbons per section (g)
- \( \rho_{oil} = \) Density of oil (g/cm^3)

To calculate the density of oil, the following conversion is assumed:

\[ \rho_{oil} = \text{Specific gravity} = \frac{141.5}{131.5 + \text{API gravity}} \]

- Step 3: calculation of barrels of oil per section:

\[ OIP = V_{Sh0+Sh1HC} \times 6.29E-6, \text{ where} \]

- \( OIP = \) target oil in place (bbl/acre-ft)
- \( V_{Sh0+Sh1HC} = \) Volume of Sh0+Sh1 hydrocarbons per section (bbl)

The OIP (bbl Oil/acre-ft) has been calculated for the available core samples based on the results obtained from both the Basic/Bulk-Rock and Shale Play methods. The results (Figure 6.6) show that the highest OIP is present in the lower Eagle Ford at Well #2 location, ranging between 145-491 bbl Oil/acre-ft. The lower portion of the upper Eagle Ford member (i.e., samples #GZ-7 and #GZ-8) at Well #1 location presents medium-to-high potential in terms of OIP where values range between 146-178 bbl Oil/acre-ft.
6.2 Organic matter type and distribution

Organic matter (OM) type and distribution in organic-rich mudrocks can be very difficult to recognize under transmitted light microscopy. This technique gives a preliminary assessment on the organic matter distribution within the rock (e.g., inside foraminifera test chambers, organic matter lenses within the matrix). In contrast, SEM yields a more precise characterization.
of the organic matter type and distribution. Therefore, SEM imaging study has been performed to primarily differentiate between in-situ organic matter and migrated organic matter. In this study, it is very important to differentiate between kerogen, bitumen, solid bitumen and pyrobitumen. Kerogen can be defined as fossilized organic material insoluble in alkaline or organic solvents that can be converted by distillation to petroleum products (Gary et al., 1977; Milliken et al., 2014). Bitumen is a liquid organic compound released by kerogen maturation as a result of diagenetic processes. In contrast with kerogen, bitumen is soluble in alkaline and organic solvents (Milliken et al., 2014). Solid bitumen is a very viscous organic compound soluble in carbon disulphide. It can originate from migrated bitumen or oil (Loucks and Reed, 2014). Pyrobitumen is considered a solid organic substance insoluble in carbon disulphide. It is originated as a result of the decomposition of bitumen or oil (secondary cracking). Upon heating, pyrobitumens yield liquid bitumens and gaseous hydrocarbon compounds (Gary et al., 1977; Jarvie et al., 2007; Speight, 2007; Loucks and Reed, 2014). Figure 6.7 describes the different intermediate byproducts as a result of kerogen maturation. Distinction between different types of organic matter on SEM images is made based on the criteria described in Loucks and Reed (2014).

Milliken et al. (2014) proposed a nomenclature for the different types of organic matter found during imaging analysis on SEM. The three types of organic matter are: 1) “detrital OM” (DOM); 2) “secondary OM” (SOM); and 3) OM of uncertain origin (UOM). The origin of DOM corresponds to detrital organic materials existent at the time of deposition (i.e. kerogen). DOM has the potential to evolve first into bitumen, followed by solid bitumen or pyrobitumen during thermal maturation (Loucks and Reed, 2014). SOM is present in mineral pores and corresponds to organic compounds generated as a result of diagenetic processes during burial. Therefore,
SOM is considered migrated organic matter. SOM may occupy the pore spaces present at the
time of hydrocarbon generation, thus reducing the former porosity present in the rock. This type
of OM can potentially develop pores during early gas generation (Milliken et al., 2014). UOM is
that organic matter for which is difficult to determine whether it is DOM or SOM.

![Source Rock Processes](image)

Figure 6.7 Flowchart showing the processes involved in the generation of bitumen, oil and
pyrobitumen in a source rock. Kerogen is first decomposed to either gas or bitumen. This stage is
followed by primary cracking which involves decomposition of bitumen to oil and gas, and
possibly to solid bitumen or pyrobitumen. Lastly, secondary cracking process may generate solid
bitumen, pyrobitumen or gas from oil decomposition. Note that solid bitumen is not included in
this figure. Biodegradation of oil may also generate gas. From Jarvie et al. (2007).

In general, a rock containing only DOM is considered a source rock. If DOM and SOM
are present, the rock can be considered a source rock and a reservoir. In contrast, presence of
microporous solid SOM and hydrocarbons is considered a reservoir rock (Milliken et al., 2014).
In this research, the three types of organic matter were identified in the available Eagle Ford rock
samples. Consequently, the Eagle Ford Shale is considered both a source rock and a reservoir,
also referred to as a self-contained source-reservoir system (Jarvie et al., 2007).

The organic matter type in the lower Eagle Ford, Well #1 is predominantly DOM (Figure
6-8). In contrast, SOM presence is rare. Where present, SOM is found in the interparticle pore
spaces inside foraminifera test chambers (Figure 6.9) and in the intergranular space of carbonate-rich fecal pellets (Figure 6.10). The imaging analysis of the lower Eagle Ford in Well #1 supports the low TOC (2.13-2.46 wt. %) and the lack of mobile hydrocarbons content within this member (2.38-2.67 mg HC/g rock). The absence of organic matter porosity (e.g. bubble-like pores) in SOM indicates lower maturity compared to the lower Eagle Ford at Well #2 location.

Lower Eagle Ford at Well #2 location presents higher TOC (3.73-8.02 wt. %) and hydrocarbons content (6.68-22.69 mg HC/g rock). This higher content in mobile hydrocarbons is supported in SEM imaging analysis by a dominant presence of SOM in the former intermineral pore space (Figure 6.11) or inside foraminifera test chambers (Figure 6.12). Well-developed bubble-like SOM porosity indicates higher hydrocarbons generation, thus higher maturity in the lower Eagle Ford in Well #2.

The upper Eagle Ford (Well #1) shows different organic matter type content and distribution at different depths. The lower portion of the upper Eagle Ford (samples #GZ-7 and #GZ-8) has a TOC between 4.91-5.86 wt. % and mobile hydrocarbons content between 6.74-8.22 mg HC/g rock. In contrast, the upper portion of this member (samples #GZ-4, #GZ-5 and #GZ-6) presents a TOC between 1.24-1.27 wt. % and mobile hydrocarbons content between 2.30-4.42 mg HC/g rock. SEM imaging study indicates that the lower portion contains higher SOM content (Figure 6.13) compared to the upper portion, which predominantly contains DOM (Figure 6-14).

The differences in SOM content match the results on mobile hydrocarbons content from Rock-Eval analysis. The higher the mobile hydrocarbons content the larger the presence of SOM in rock samples. This indicates different thermal maturation history between Well #1 and Well #2 locations. The lower Eagle Ford member at Well #2 location shows a more intense
hydrocarbon generation and therefore higher maturity compared to the upper and lower Eagle Ford members at Well #1 location.
Figure 6-8. SEM photomicrographs of organic matter type and distribution in the lower Eagle Ford. Ar-ion milled sample. BSE image. (A) DOM is identified based on discrete particle shapes. SOM may be found partially filling the interparticle pore spaces inside foraminifera test chambers. Yellow box indicates area of image B. 1,000x magnification. (B) Higher-magnification view of the image area indicated in (A). DOM can also be present intermixed with minerals in the rock matrix as organic matter aggregates. Note the ductile character of the non-discrete particulate shape DOM. Possible wood fragment is identified based on the arcuate edges (Milliken et al., 2013). SOM fills the former available pore space between clays (kaolinite) inside a foraminifera test chamber. Red arrows indicate porosity inside the DOM (top left corner) and SOM (lower third part, inside test chamber). 2,000x magnification. Sample GZ-10, Well #1.
Figure 6.9  SEM photomicrographs of organic matter type and distribution in the lower Eagle Ford. Ar-ion milled sample, BSE image. (A) This image illustrates the low organic matter content in the lower Eagle Ford at Well #1 location. Where present, SOM is partially filling the interparticle pore space within the matrix. Red arrows indicate devolatilization cracks. Yellow box indicates area of image B. 1,100x magnification. (B) Higher-magnification view of the image area indicated in (A). DOM is present in the matrix occupying the interparticle space in the rock matrix. SOM is almost absent. Red arrows indicate intercrystalline porosity. 3,500x magnification. Sample GZ-10, Well #1.
Figure 6.10  Close-up SEM photomicrograph of carbonate-rich fecal pellet in the lower Eagle Ford. Ar-ion milled sample. BSE image. Homogeneous DOM without pore development is present on top of the fecal pellet. Note the ductile character of the DOM. No pore space is present between mineral grains and the DOM. SOM is present in the intergranular pore space inside the fecal pellet. The porosity in the SOM (red arrows) is most likely created as a result of devolatilization. 3,500x magnification. Lower Eagle Ford, sample #GZ-9, Well #1.
Figure 6.11  SEM photomicrographs of organic matter type and distribution in the lower Eagle Ford. Ar-ion milled sample. BSE image. (A) Abundant porous SOM is present in the matrix filling the former intermineral pore space. Yellow box indicates area of image B. 2,000x magnification. (B) The SOM shows spongy texture as a result of organic matter pore development. This indicates higher thermal maturation than both the lower Eagle Ford in Well #1 and upper part of the upper Eagle Ford. The SOM overlies the crystals, evidencing that migration of bitumen or oil occurred into the former intercrystalline pore space. 6,500x magnification. Sample #LS-5.
Figure 6.12  SEM photomicrographs of organic matter type and distribution of the lower Eagle Ford. Ar-ion milled sample. (A) The chambers of the foraminifera are filled with SOM, probably solid bitumen. Early calcite crystals and pyrite frambooids formed first, followed by organic matter migration (SOM) inside the test chambers located on the right. The left test chamber shows authigenic kaolinite that precipitated in the intraparticle pore space before organic matter migration (SOM) occurred. These compositional differences inside the foraminifera test chambers in such small distances show the complexity of the diageneric processes in the Eagle Ford. Red arrows indicate organic matter porosity. 2,000x magnification. (B) BSE image of A. Sample #LS-2.
Figure 6.13  SEM photomicrographs of organic matter type and distribution in the upper Eagle Ford. Ar-ion milled sample. BSE image. (A) Abundant carbonate-rich fecal pellets are present in this interval. Most of these fecal pellets are deformed due to compaction. The fecal pellets contain SOM in the intergranular space, similar to that observed in Figure 6.10. Some of the foraminifera test chambers are cemented with calcite, while others are filled with kaolinite and SOM. Yellow box indicates area of image B. 330x magnification. (B) Close-up image of the kaolinite-SOM mixture inside a foraminifera test chamber. SOM (solid bitumen or pyrobitumen) is present in the former pore space existent between kaolinite (k) crystals. The SOM seems to overlay the kaolinite booklets. This indicates that the organic matter migrated as a fluid, presumably bitumen or oil into the foraminifera chamber once the kaolinite booklets were formed. Red arrows indicate aligned porosity within the SOM, presumably originated as a result of volatilization. 5,000x magnification. Sample #GZ-8, Well #1.
Figure 6-14. SEM photomicrographs of organic matter distribution in the upper Eagle Ford. Ar-ion milled sample. (A) Image of the upper Eagle Ford, where organic matter is practically absent compared to upper intervals in the same member. Yellow box indicates area of image B. 1,000x magnification. (B) Close-up image of area indicated in (A). Organic matter is classified as SOM based on the existing pore spaces (red arrows) between the organic matter and the surrounding mineral grains. This pore space is indicative that the SOM presumably corresponds to solid bitumen. 3,700x magnification. Sample #GZ-5.
CHAPTER 7

CONCLUSIONS

1. Thorium response on spectral gamma ray logs is a good indicator to define the boundary between the lower and upper Eagle Ford members. This difference in thorium response is primarily due the kaolinite content (wt. %) in the rock. The higher the kaolinite content, the higher the thorium response.

2. Eight facies and six microfacies were recognized in the Eagle Ford Shale based on XRD data and fossil abundance.

3. In general, transgressive events are associated with deep-marine anoxic conditions. Nonetheless, the high abundance of benthonic organisms in the lower Eagle Ford at Well #2 location suggests that transgressive events do not necessarily imply the aforementioned environmental conditions.

4. The high heterogeneity of microfacies at millimeter scale and the presence of carbonate laminae and other aggregates increase the permeability anisotropy of the rock.

5. Water immersion porosimetry overstates porosity when clay content in the rock is larger than 50 wt. %. In contrast, mercury injection capillary pressure is not strongly affected by the mineralogical composition of the rock, and therefore it offers more reliable total porosity results.

6. Mercury injection capillary pressure provides accurate data on pore throat size distribution in mudrocks. Nonetheless, the permeability results obtained from this method are not completely reliable as they are calculated based on a correlation developed for other type of rocks (e.g., sandstones).

7. Pore throat diameters are primarily within the nanopore and micropore size ranges.
8. Interparticle pores are not abundant in the Eagle Ford. The dominant pore-type is intraparticle pore within the organic matter.

9. Mercury injection capillary pressure results indicate that the permeability of the analyzed samples increases with increasing total porosity. This correlation suggests that the porosity in samples with higher permeability values (lower Eagle Ford, Well #2) has to be effective porosity. In these samples, the majority of the pores are intraparticle organic matter pores based on SEM imaging study. This suggests that the intraparticle organic matter porosity creates a 3D pore network that contributes to an increase in permeability of the rock.

10. The Eagle Ford Shale is a kerogen type II marine oil-prone source rock. The lower Eagle Ford at Well #2 location shows higher maturity and oil and gas generation than the upper and lower Eagle Ford members at Well #1 location.

11. The IFPEN Shale Play method is the most efficient geochemical analysis to evaluate hydrocarbon potential in shale oil and gas plays. This method shows an average increase of 25.69 % hydrocarbon content over the Basic/Bulk-Rock method.

12. The lower Eagle Ford at Well #2 location presents higher hydrocarbon content (6.68-22.69 mg HC/g rock) compared to the lower Eagle Ford at Well #1 location (2.38-2.67 mg HC/g rock) based on Rock-Eval results.

13. The lower portion of the upper Eagle Ford (samples #GZ-7 and #GZ-8) presents higher hydrocarbon content (6.74-8.22 mg HC/g rock) than the lower Eagle Ford at the same well location (2.38-2.67 mg HC/g rock) based on Rock-Eval results. These hydrocarbons could have migrated up-dip from the lower Eagle Ford member or generated in-situ.

14. Secondary organic matter is dominant in the lower Eagle Ford (Well #2) and lower portion of the upper Eagle Ford (Well #1). This indicates a more intense generation of hydrocarbons
and subsequent migration compared to those samples where detrital organic matter is dominant.

15. Unhealed microfractures were not recognized in any of the analyzed samples on SEM. Instead, healed microfractures representing two different diagenetic stages were recognized on petrographic thin sections. When hydraulic fracturing the rock, these healed microfractures or calcite veins represent preferential pathways for the induced fractures to follow. Also, they might have contributed to hydrocarbon migration before they healed, especially the Type II (post-diagenetic) microfracture.
CHAPTER 8

FUTURE WORK

1. Compare the upper Eagle Ford member characteristics at different locations along the Eagle Ford play area (e.g., hydrocarbons content, mineralogy).

2. Perform water immersion porosimetry with different saturating fluids such as kerogen. This will help to compare results and evaluate the applicability of this method in the Eagle Ford Shale.

3. Perform different experiments and methods to quantitatively obtain more porosity data, such as nitrogen adsorption and nuclear magnetic resonance (NMR).

4. Identification of unhealed natural microfractures that might contribute to hydrocarbons migration by using different techniques such as cathodoluminiscence or computed tomography (CT) scan.

5. Determine the origin (i.e., biogenic or detrital) and quantities of silica within the Eagle Ford Shale. Zones with high biogenic quartz will influence in reservoir characteristics affecting porosity, brittleness and log response (Ratcliffe et al., 2012). X-ray fluorescence (XRF) should be conducted to determine whether the quartz present in the Eagle Ford Shale is detrital or biogenic in origin.

6. Study the paragenesis of the upper and Lower Eagle Ford members to better understand the reason behind some foraminifera have their test chambers cemented with calcite while others are filled with kaolinite and organic matter.

7. Study the effect of the ash layers (facies 8: claystone) found in the Eagle Ford Shale during hydraulic fracturing.
8. Perform gas chromatography to study the composition of the hydrocarbons and determine potential migration between Eagle Ford members, and Austin Chalk and Buda Limestone.
LIST OF SYMBOLS AND ACRONYMS

%  Percent
°C  Degree Celsius
µm  Micrometers
API  American Petroleum Institute
Ar  Argon
BOPD  Barres of Oil Per Day
C  Carbon
CFPD  Cubic Feet Per Day
Cl  Chlorine
cm  Centimeters
cm³  Cubic centimeters
DOM  Detrital Organic Matter
ESEM  Environmental Scanning Electron Microscopy
FE-SEM  Field Emission Scanning Electron Microscopy
FID  Flame Ionization Detector
ft  Feet
g  Gram(s)
GRI  Gas Research Institute
h  Hour
H  Hydrogen
HC  Hydrocarbon(s)
Hg  Mercury
HI  Hydrogen Index
IFPEN  Institut Français du Pétrole Energies Nouvelles
in  Inches
K  Potassium
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>Meters</td>
</tr>
<tr>
<td>Ma</td>
<td>Million years ago</td>
</tr>
<tr>
<td>MCU</td>
<td>Mid-Cretaceous Unconformity</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>mi²</td>
<td>Squared Miles</td>
</tr>
<tr>
<td>MICP</td>
<td>Mercury Injection Capillary Pressure</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeters</td>
</tr>
<tr>
<td>nd</td>
<td>Nanodarcy</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>ϕ</td>
<td>Porosity</td>
</tr>
<tr>
<td>OI</td>
<td>Oxygen Index</td>
</tr>
<tr>
<td>OIP</td>
<td>Oil-In-Place</td>
</tr>
<tr>
<td>OM</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>QEMSCAN</td>
<td>Quantitative Evaluation of Minerals by SCANning electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SOM</td>
<td>Secondary Organic Matter</td>
</tr>
<tr>
<td>Th</td>
<td>Thorium</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>U</td>
<td>Uranium</td>
</tr>
<tr>
<td>UOM</td>
<td>Organic Matter of Uncertain Origin</td>
</tr>
<tr>
<td>WIP</td>
<td>Water Immersion Porosimetry</td>
</tr>
<tr>
<td>WIS</td>
<td>Western Interior Seaway</td>
</tr>
<tr>
<td>Wt. %</td>
<td>Weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
</tr>
</tbody>
</table>
REFERENCES CITED


APPENDIX A

Table A.1  XRD analysis results from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Quartz (wt.%)</th>
<th>Calcite (wt.%)</th>
<th>Dolomite (wt.%)</th>
<th>Mica + Illite (wt.%)</th>
<th>Kaolinite (wt.%)</th>
<th>Chlorite (wt.%)</th>
<th>Plagioclase (wt.%)</th>
<th>K-feldspar (wt.%)</th>
<th>Pyrite (wt.%)</th>
<th>Apatite (wt.%)</th>
<th>Anamorphos (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-1</td>
<td>4</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-2</td>
<td>4</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-3</td>
<td>4</td>
<td>87</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-4</td>
<td>8</td>
<td>83</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-5</td>
<td>15</td>
<td>63</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-6</td>
<td>13</td>
<td>68</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-6'</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>50</td>
<td>9</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>GZ-7</td>
<td>18</td>
<td>55</td>
<td>0</td>
<td>17</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-7&quot;</td>
<td>6</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-8</td>
<td>16</td>
<td>57</td>
<td>0</td>
<td>12</td>
<td>7</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-9</td>
<td>20</td>
<td>8</td>
<td>0</td>
<td>30</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-10</td>
<td>24</td>
<td>13</td>
<td>0</td>
<td>35</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>GZ-11</td>
<td>5</td>
<td>88</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-12</td>
<td>11</td>
<td>25</td>
<td>0</td>
<td>48</td>
<td>10</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GZ-13</td>
<td>10</td>
<td>46</td>
<td>10</td>
<td>21</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>LS-1</td>
<td>16</td>
<td>66</td>
<td>1</td>
<td>6</td>
<td>5</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LS-2</td>
<td>28</td>
<td>53</td>
<td>2</td>
<td>9</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LS-3</td>
<td>24</td>
<td>45</td>
<td>0</td>
<td>17</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LS-4</td>
<td>21</td>
<td>63</td>
<td>0</td>
<td>9</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LS-5</td>
<td>17</td>
<td>66</td>
<td>1</td>
<td>9</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table A.2  Water immersion porosimetry results from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Before Drying (g)</th>
<th>After Drying (g)</th>
<th>Air Average (g)</th>
<th>Immeresed Average (g)</th>
<th>Water-saturated bulk density (ps) (g/cm³)</th>
<th>Anhydrous grain density (pa) (g/cm³)</th>
<th>Total Porosity (p=s) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-2</td>
<td>2.60</td>
<td>2.60</td>
<td>2.60</td>
<td>2.59</td>
<td>2.63</td>
<td>1.58</td>
<td>2.55</td>
</tr>
<tr>
<td>GZ-3</td>
<td>2.66</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
<td>2.67</td>
<td>1.64</td>
<td>2.63</td>
</tr>
<tr>
<td>GZ-4</td>
<td>2.35</td>
<td>2.52</td>
<td>2.52</td>
<td>2.52</td>
<td>2.58</td>
<td>2.18</td>
<td>2.61</td>
</tr>
<tr>
<td>GZ-5</td>
<td>2.81</td>
<td>2.79</td>
<td>2.79</td>
<td>2.79</td>
<td>2.84</td>
<td>2.74</td>
<td>2.62</td>
</tr>
<tr>
<td>GZ-6</td>
<td>3.56</td>
<td>3.53</td>
<td>3.53</td>
<td>3.53</td>
<td>3.59</td>
<td>2.19</td>
<td>2.61</td>
</tr>
<tr>
<td>GZ-7</td>
<td>4.78</td>
<td>4.72</td>
<td>4.72</td>
<td>4.72</td>
<td>5.02</td>
<td>2.89</td>
<td>2.40</td>
</tr>
<tr>
<td>GZ-8</td>
<td>2.70</td>
<td>2.66</td>
<td>2.66</td>
<td>2.66</td>
<td>2.83</td>
<td>1.62</td>
<td>2.37</td>
</tr>
<tr>
<td>GZ-9</td>
<td>6.24</td>
<td>6.15</td>
<td>6.15</td>
<td>6.14</td>
<td>6.21</td>
<td>3.72</td>
<td>2.54</td>
</tr>
<tr>
<td>GZ-10</td>
<td>4.65</td>
<td>4.59</td>
<td>4.59</td>
<td>4.59</td>
<td>4.64</td>
<td>2.80</td>
<td>2.56</td>
</tr>
<tr>
<td>LS-1</td>
<td>1.75</td>
<td>1.74</td>
<td>1.74</td>
<td>1.73</td>
<td>1.76</td>
<td>1.08</td>
<td>1.26</td>
</tr>
<tr>
<td>LS-2</td>
<td>2.62</td>
<td>2.60</td>
<td>2.60</td>
<td>2.59</td>
<td>2.61</td>
<td>1.59</td>
<td>2.61</td>
</tr>
<tr>
<td>LS-3</td>
<td>1.97</td>
<td>1.96</td>
<td>1.96</td>
<td>1.96</td>
<td>1.97</td>
<td>1.20</td>
<td>2.61</td>
</tr>
<tr>
<td>LS-4</td>
<td>1.97</td>
<td>1.96</td>
<td>1.96</td>
<td>1.96</td>
<td>1.97</td>
<td>1.20</td>
<td>2.61</td>
</tr>
<tr>
<td>LS-5</td>
<td>1.97</td>
<td>1.96</td>
<td>1.96</td>
<td>1.96</td>
<td>1.97</td>
<td>1.20</td>
<td>2.61</td>
</tr>
</tbody>
</table>

* Density of the saturation and immersion fluid (3% KCl deionized water) is 1.018525 g/cm³.
Table A.3 MICP data and permeability results from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Median Pore Throat Diameter (µm)</th>
<th>MICP Porosity (%)</th>
<th>Calc MICP Permeability (µd)</th>
<th>MICP Bulk Density (g/cm³)</th>
<th>MICP Grain Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>0.00800</td>
<td>0.80</td>
<td>0.00443</td>
<td>2.66</td>
<td>2.67</td>
</tr>
<tr>
<td>GZ-5</td>
<td>0.01353</td>
<td>1.41</td>
<td>0.02647</td>
<td>2.71</td>
<td>2.73</td>
</tr>
<tr>
<td>GZ-6</td>
<td>0.01300</td>
<td>0.32</td>
<td>0.00260</td>
<td>2.68</td>
<td>2.68</td>
</tr>
<tr>
<td>GZ-7</td>
<td>0.01150</td>
<td>4.63</td>
<td>0.10078</td>
<td>2.60</td>
<td>2.72</td>
</tr>
<tr>
<td>GZ-8</td>
<td>0.00863</td>
<td>3.55</td>
<td>0.05219</td>
<td>2.55</td>
<td>2.63</td>
</tr>
<tr>
<td>GZ-9</td>
<td>0.00870</td>
<td>3.57</td>
<td>0.04691</td>
<td>2.62</td>
<td>2.69</td>
</tr>
<tr>
<td>GZ-10</td>
<td>0.00730</td>
<td>3.73</td>
<td>0.03831</td>
<td>2.55</td>
<td>2.63</td>
</tr>
<tr>
<td>LS-1</td>
<td>0.01972</td>
<td>8.24</td>
<td>0.86467</td>
<td>2.34</td>
<td>2.54</td>
</tr>
<tr>
<td>LS-2</td>
<td>0.01600</td>
<td>10.27</td>
<td>0.86401</td>
<td>2.34</td>
<td>2.58</td>
</tr>
<tr>
<td>LS-3</td>
<td>0.01210</td>
<td>8.11</td>
<td>0.31316</td>
<td>2.35</td>
<td>2.55</td>
</tr>
<tr>
<td>LS-4</td>
<td>0.01770</td>
<td>8.40</td>
<td>0.62229</td>
<td>2.37</td>
<td>2.58</td>
</tr>
<tr>
<td>LS-5</td>
<td>0.01000</td>
<td>3.34</td>
<td>0.03737</td>
<td>2.57</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Figure A.1a Sample #GZ-4 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.1b  Sample #GZ-5 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Figure A.1c  Sample #GZ-6 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.1d  Sample #GZ-7 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Figure A.1e  Sample #GZ-8 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.1f  Sample #GZ-9 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Figure A.1g  Sample #GZ-10 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.1h  Sample #LS-1 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Figure A.1i  Sample #LS-2 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.1j  Sample #LS-3 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Figure A.1k  Sample #LS-4 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.
Figure A.11 Sample #LS-5 dSw/dLog pore size and Hg (nwp) saturation vs log pore radius plot.

Table A.4 Rock-Eval results from Basic/Bulk-Rock method from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>TOC (wt. %)</th>
<th>S₁ (mgHC/g)</th>
<th>S₂ (mgHC/g)</th>
<th>S₃ (mgHC/g)</th>
<th>Tmax (°C)</th>
<th>HI (mgHC/gTOC)</th>
<th>OI (mgCO₂/gTOC)</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>1.22</td>
<td>3.15</td>
<td>3.15</td>
<td>0.39</td>
<td>438</td>
<td>258</td>
<td>32</td>
<td>0.50</td>
</tr>
<tr>
<td>GZ-6</td>
<td>1.25</td>
<td>2.71</td>
<td>2.96</td>
<td>0.25</td>
<td>440</td>
<td>238</td>
<td>20</td>
<td>0.38</td>
</tr>
<tr>
<td>GZ-7</td>
<td>1.55</td>
<td>5.00</td>
<td>4.15</td>
<td>0.28</td>
<td>440</td>
<td>269</td>
<td>18</td>
<td>0.40</td>
</tr>
<tr>
<td>GZ-8</td>
<td>5.79</td>
<td>6.00</td>
<td>15.34</td>
<td>0.32</td>
<td>445</td>
<td>265</td>
<td>6</td>
<td>0.28</td>
</tr>
<tr>
<td>GZ-9</td>
<td>4.88</td>
<td>1.41</td>
<td>5.79</td>
<td>0.23</td>
<td>446</td>
<td>269</td>
<td>6</td>
<td>0.28</td>
</tr>
<tr>
<td>GZ-10</td>
<td>2.15</td>
<td>1.84</td>
<td>6.74</td>
<td>0.30</td>
<td>444</td>
<td>275</td>
<td>11</td>
<td>0.20</td>
</tr>
<tr>
<td>LS-1</td>
<td>6.69</td>
<td>16.98</td>
<td>11.64</td>
<td>0.46</td>
<td>443</td>
<td>175</td>
<td>7</td>
<td>0.59</td>
</tr>
<tr>
<td>LS-2</td>
<td>7.68</td>
<td>18.55</td>
<td>14.73</td>
<td>0.34</td>
<td>442</td>
<td>192</td>
<td>5</td>
<td>0.56</td>
</tr>
<tr>
<td>LS-3</td>
<td>7.90</td>
<td>9.30</td>
<td>13.27</td>
<td>0.29</td>
<td>443</td>
<td>168</td>
<td>4</td>
<td>0.41</td>
</tr>
<tr>
<td>LS-4</td>
<td>5.86</td>
<td>9.35</td>
<td>11.83</td>
<td>0.47</td>
<td>441</td>
<td>202</td>
<td>8</td>
<td>0.44</td>
</tr>
<tr>
<td>LS-5</td>
<td>3.67</td>
<td>5.02</td>
<td>6.91</td>
<td>0.35</td>
<td>444</td>
<td>189</td>
<td>10</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*PI – Production Index, \( PI = \frac{S_1}{S_1 + S_2} \)
Table A.5  Rock-Eval results from IFPEN Shale Play method from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>TOC (wt. %)</th>
<th>Sh0 (mgHC/g)</th>
<th>Sh1 (mgHC/g)</th>
<th>Sh2 (mgHC/g)</th>
<th>Tmax (°C)</th>
<th>Sh2</th>
<th>HI (mgHC/gTOC)</th>
<th>OI (mgCO2/gTOC)</th>
<th>PIShale</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>1.27</td>
<td>2.45</td>
<td>1.97</td>
<td>2.77</td>
<td>440</td>
<td>218</td>
<td>9</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>GZ-5</td>
<td>1.24</td>
<td>1.11</td>
<td>1.19</td>
<td>2.68</td>
<td>439</td>
<td>216</td>
<td>6</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>GZ-6</td>
<td>1.57</td>
<td>1.85</td>
<td>1.70</td>
<td>3.73</td>
<td>440</td>
<td>237</td>
<td>8</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>GZ-7</td>
<td>5.86</td>
<td>3.51</td>
<td>4.71</td>
<td>14.14</td>
<td>443</td>
<td>242</td>
<td>2</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>GZ-8</td>
<td>4.91</td>
<td>3.01</td>
<td>3.73</td>
<td>11.75</td>
<td>445</td>
<td>239</td>
<td>2</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>GZ-9</td>
<td>2.13</td>
<td>0.57</td>
<td>1.81</td>
<td>5.06</td>
<td>445</td>
<td>237</td>
<td>4</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>GZ-10</td>
<td>2.46</td>
<td>0.69</td>
<td>1.98</td>
<td>6.11</td>
<td>446</td>
<td>249</td>
<td>4</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>LS-1</td>
<td>6.79</td>
<td>9.38</td>
<td>11.19</td>
<td>9.74</td>
<td>442</td>
<td>143</td>
<td>2</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>LS-2</td>
<td>7.78</td>
<td>10.49</td>
<td>12.21</td>
<td>11.96</td>
<td>442</td>
<td>154</td>
<td>2</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>LS-3</td>
<td>8.02</td>
<td>5.06</td>
<td>7.53</td>
<td>11.00</td>
<td>443</td>
<td>137</td>
<td>1</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>LS-4</td>
<td>5.88</td>
<td>5.17</td>
<td>7.28</td>
<td>9.41</td>
<td>442</td>
<td>160</td>
<td>3</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>LS-5</td>
<td>3.73</td>
<td>2.67</td>
<td>4.02</td>
<td>5.87</td>
<td>443</td>
<td>157</td>
<td>3</td>
<td>0.53</td>
<td></td>
</tr>
</tbody>
</table>

*PIShale – Production Index of Shale Plays, \( P_{IShale} = \frac{Sh0+Sh1}{Sh0+Sh1+Sh2} \)

Table A.6  OIP intermediate calculations based on results obtained from Basic/Bulk-Rock method from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>S1 (mg HC/ g rock)</th>
<th>MS1HHC (g)</th>
<th>Volume of oil per section (bbl)</th>
<th>OOIP (bbl Oil/acre-ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>3.15</td>
<td>22</td>
<td>4376</td>
<td>68</td>
</tr>
<tr>
<td>GZ-5</td>
<td>1.84</td>
<td>13</td>
<td>2549</td>
<td>40</td>
</tr>
<tr>
<td>GZ-6</td>
<td>2.71</td>
<td>19</td>
<td>3765</td>
<td>59</td>
</tr>
<tr>
<td>GZ-7</td>
<td>6.00</td>
<td>42</td>
<td>8335</td>
<td>130</td>
</tr>
<tr>
<td>GZ-8</td>
<td>5.00</td>
<td>35</td>
<td>6939</td>
<td>108</td>
</tr>
<tr>
<td>GZ-9</td>
<td>1.41</td>
<td>10</td>
<td>1959</td>
<td>31</td>
</tr>
<tr>
<td>GZ-10</td>
<td>1.84</td>
<td>13</td>
<td>2556</td>
<td>40</td>
</tr>
<tr>
<td>LS-1</td>
<td>16.98</td>
<td>118</td>
<td>23587</td>
<td>368</td>
</tr>
<tr>
<td>LS-2</td>
<td>18.55</td>
<td>128</td>
<td>25761</td>
<td>402</td>
</tr>
<tr>
<td>LS-3</td>
<td>9.30</td>
<td>64</td>
<td>12912</td>
<td>201</td>
</tr>
<tr>
<td>LS-4</td>
<td>9.35</td>
<td>65</td>
<td>12981</td>
<td>202</td>
</tr>
<tr>
<td>LS-5</td>
<td>5.02</td>
<td>35</td>
<td>6973</td>
<td>109</td>
</tr>
</tbody>
</table>
Table A.7 OIP intermediate calculations based on results obtained from IFPEN Shale Play method from Well #1 and Well #2 samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sh0+Sh1 (mg HC/ g rock)</th>
<th>MSh0+Sh1HC (g)</th>
<th>Volume of oil per section (bbl)</th>
<th>OOIP (bbl Oil/acre-ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-4</td>
<td>4.42</td>
<td>31</td>
<td>6133</td>
<td>96</td>
</tr>
<tr>
<td>GZ-5</td>
<td>2.30</td>
<td>16</td>
<td>3188</td>
<td>50</td>
</tr>
<tr>
<td>GZ-6</td>
<td>3.55</td>
<td>25</td>
<td>4924</td>
<td>77</td>
</tr>
<tr>
<td>GZ-7</td>
<td>8.22</td>
<td>57</td>
<td>11412</td>
<td>178</td>
</tr>
<tr>
<td>GZ-8</td>
<td>6.74</td>
<td>47</td>
<td>9356</td>
<td>146</td>
</tr>
<tr>
<td>GZ-9</td>
<td>2.38</td>
<td>16</td>
<td>3299</td>
<td>51</td>
</tr>
<tr>
<td>GZ-10</td>
<td>2.67</td>
<td>18</td>
<td>3702</td>
<td>58</td>
</tr>
<tr>
<td>LS-1</td>
<td>20.56</td>
<td>142</td>
<td>28561</td>
<td>445</td>
</tr>
<tr>
<td>LS-2</td>
<td>22.69</td>
<td>157</td>
<td>31519</td>
<td>491</td>
</tr>
<tr>
<td>LS-3</td>
<td>12.59</td>
<td>87</td>
<td>17489</td>
<td>273</td>
</tr>
<tr>
<td>LS-4</td>
<td>12.45</td>
<td>86</td>
<td>17288</td>
<td>270</td>
</tr>
<tr>
<td>LS-5</td>
<td>6.68</td>
<td>46</td>
<td>9279</td>
<td>145</td>
</tr>
</tbody>
</table>