


# THERMAL MATURITY, COMPOSITION, AND ORIGIN OF THE HYDROCARBON GASES OF THE EAGLE FORD SHALE IN TEXAS, USA

Senior Thesis  
Submitted in partial fulfillment of the requirements for the  
Bachelor of Science Degree  
At The Ohio State University

By

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2017

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A handwritten signature in blue ink, appearing to read "Tom Darrah", is written over a solid black horizontal line.

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## **ABSTRACT**

The Eagle Ford Shale, a high-growth and profitable developing play, locates mainly in South Texas. Even though it has been actively developed for about 9 years, to reduce industrial exploitation risk, properties of the fluids in the Eagle Ford Shale still need to be studied. In this research, samples of oil and associated gases collected from 27 hydraulically fractured horizontal commercial wells were analyzed for major gas compositions and stable carbon isotopic ratios to characterize the natural gases of the Eagle Ford Shale.

The experimental data suggest that natural gases of the Eagle Ford Shale are thermogenic, oil-associated wet gas in early stage of thermal maturity for four reasons: 1) large amount of ethane and heavier aliphatic hydrocarbons ( $0.11 \leq C_2+/C_1 \leq 1.4$ ); 2) the stable carbon isotopic composition of methane and ethane ( $-48 < \delta^{13}C_1 (\text{‰}) < -36$  and  $-36.7 < \delta^{13}C_2 (\text{‰}) < -33.93$ ); 3) vitrinite reflectance values ( $0.61 < R_o < 0.96$ ) calculated from carbon isotope ratios of methane and ethane using two individual equations developed by Whiticar et al., 1994; 4) the sublinear nature of Chung Plot.

## **ACKNOWLEDGEMENTS**

I would like to thank Dr. Terry Wilson, Dr. Christina Millan, and Dr. Dan Kelley for showing me how wonderful it is to be a geologist in field camp. Many thanks to Connor Gallagher, Erica Maletic, Tricia Hall, and Will Blocher for their assistance and thoughtfulness about both school work and life. Special thanks to my incredible mapping partners, my considerate roommates, and all of the other awesome fellow students for an unforgettable 6-weeks in Utah.

I would like to thank all the teachers, teaching assistants, and professors from kindergarten to college who tolerated my innumerable stupid questions. And special thanks to whoever made politics – my least favorite subject, a required course in every Chinese middle school, high school, and college. Without this requirement, I would have never thought about studying abroad.

I would like to thank Mr. Jacob Harrington, Mr. Myles Moore, Mr. Yohei Matsui, and Mr. Colin Whyte for their hard work in sample collection and analyses. Thanks to the National Science Foundation EAGER (1249255) and SusChEM (1441497) grants for financial support that benefitted this project. Most importantly, thanks to Cabot Oil and Gas Corporation for allowing this project to go forward and provided geological information about the area.

Also, I would like to take this opportunity to express my sincere thanks to my parents (even though they do not speak English at all) for their support, guidance, and understanding on everything in my life. Special thanks to my dog, Aozai, who has always kept my parents from being lonely while their only child has been on the opposite side of the world. Another special thanks to Zixuan Zhao, who studies Mechanical Engineering in Penn State because of me (long story), for our everlasting friendship.

Finally, I am grateful to have Dr. Tom Darrah, who probably thought I forgot him as he read through this page, be my thesis advisor and mentor to the petroleum industry. He is intelligent and humorous, and his guidance and patience gives me hope (No.1 ingredient for finishing a thesis).

## **INTRODUCTION**

Over the past decade, the combination of horizontal drilling and hydraulic fracturing have been incorporated into onshore unconventional hydrocarbon energy extraction to the extent that the United States has become a net petroleum exporter since 2014 (Vengosh et al., 2014). The advancement of these techniques has allowed for the development of new economical petroleum resources and for the collection of samples from areas that were previously inaccessible (Darrah et al., 2014). In particular, the development of unconventional horizontal drilling and hydraulic fracturing has led to the rapid increase in the volume of petroleum fluids extracted from hydrocarbon source rocks such as black shale (Darrah, et al., 2014). Access to black shales can provide exciting new information about the geology of many important petroleum basins.

Throughout the last decade, the Eagle Ford Shale, located in southern Texas, has become one of the most economically important unconventional hydrocarbon energy developments in the world (Tian et al., 2012). Between January and October 2014, the amount of oil and wet gas produced from the Eagle Ford Shale is approximately 955,000 barrels of oil per day and greater than 4,600 ft<sup>3</sup> wet gas per day (Texas Railroad Commission, 2014).

To reduce production risks, companies have conducted a lot of research on the thermal maturity of the Eagle Ford Shale at the exploration stage to analyze kerogen as either oil-prone or gas-prone, particularly within the wet-gas areas (Texas Railroad Commission, 2014). Because of the complex structural and tectonic history of this entire region, there is great local diversity in the type of petroleum and in production strategies (Tian et al., 2012).

To gain an understanding of the geological complexities, the Darrah research laboratory collected 27 samples from actively-producing commercial wells located in the Eagle Ford Shale in 2014. Previous work has examined the noble gas geochemistry of the Eagle Ford Shale (Harrington,

2015) and here, I will expand on those findings with an examination of the major ( $\text{CO}_2$ ) and hydrocarbon gas (methane (C1), ethane (C2), propane (C3), butane (C4), and pentane (C5)) chemistry in addition to the stable isotopes of hydrocarbons ( $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  of C1, C2, and C3). Data and interpretations from this study will likely contribute to a better understanding of petroleum production from the Eagle Ford Shale and the geology of this region.

## **OBJECTIVES**

The overall purpose of this study is to use noble gas geochemistry and stable isotopes to determine the source of the hydrocarbon gases in the Eagle Ford Shale. Steps applied are described below:

- Collection of oil and gas samples in the study area
- Analysis of all samples for major gas composition
- Analysis of all samples for stable carbon isotopic composition
- Determination of the source of hydrocarbon gases
- Calculation of the vitrinite reflectance (% Ro) and determination of the thermal maturity of the Eagle Ford Shale in the study area



## **BACKGROUND**

### **Geological Background**

This study focuses on the Eagle Ford Shale in Atascosa, Frio, and La Salle Counties in the Western Gulf Province, Texas, United States. Geographically, the study area is northwest of the Sligo Reef Margin, east of the Maverick Basin, south of the Ouachita Belt, and southwest of the San Marcos Arch (Figure 1) (Hentz and Ruppel, 2010). During the transgression stages of the Cretaceous Epeiric Sea in North America, argillaceous mudrock (shale) and limestone (chalk) deposited and became the Eagle Ford Shale and Austin Chalk formations, respectively (Robison, 1997). Due to the significant alterations caused by several major tectonic and structural events, the Eagle Ford Shale has become a complex petroleum play which is different from other conventional reservoirs due to its exceptionally low permeability and carbonate-rich lithology.

Stratigraphically, rock units considered as part of the study area include the Upper Cretaceous (Turonian to Cenomanian) aged Eagle Ford Shale with an average thickness of about 200 m (660 ft.) (Hentz and Ruppel, 2010). The Eagle Ford Shale overlies the Cenomanian aged Buda Limestone (a thick, micritic wackestone), and is unconformably overlain by the famous Coniancian to Campanian aged Austin Chalk (another thick limestone) (Robison, 1997) (Figure 1). Regionally, the Del Rio Shale is another argillaceous mudrock formation analogous to the Eagle Ford Shale and the Georgetown Limestone constitutes a platform carbonates formation analogous to the Austin Chalk. Both formations are Cenomanian in age and lie below the Buda Limestone in sequence (Hentz and Ruppel, 2010).

The Eagle Ford Shale itself is generally divided into two members: a lower, organic-rich mudstone, called the Britton/Pepper Shale, and an upper, more calcareous member (organic deficient), known as the Acadia Park Formation (Treadgold et al., 2011). The Kamp Ranch

Limestone is the internal carbonate marker between the lower and upper members of the Eagle Ford Shale (Treadgold et al., 2011). This division was defined by distinct changes in gamma-ray readings (thorium and uranium components). While the lower shale member contains notably higher gamma-ray values than the upper shale member due to a higher volume of bentonite and organic content, there is also a thin carbonate layer sitting between the two members where gamma-ray readings are remarkably lower than both lower and upper member (Tian et al., 2012). Similarly, gamma-ray values of the adjacent formations (Buda Limestone and Austin Chalk) are much smaller than those of the two members of the Eagle Ford Shale (Denne et al., 2014).

		Maverick basin and San Marcos arch	East Texas basin	
Upper Cretaceous	Coniacian, Santonian, Campanian	Austin Chalk	Austin Group	
	Turonian	Eagle Ford Shale	Eagle Ford Group	
			Pepper Shale	
			Woodbine Group	
	Cenomanian		Maness Shale	
			Buda Limestone	Buda Limestone
			Del Rio Shale	Del Rio (Grayson) Sh.
Georgetown Ls.			Georgetown Ls.	

Figure 1. Traditional stratigraphic column of the Eagle Ford Shale in study area and East Texas Basin made by Hentz and Ruppel (Hentz and Ruppel, 2010).

The formation of the Eagle Ford Shale began after the Cretaceous Interior Seaway merged into the growing Gulf of Mexico (Robison, 1997). Generally, the deposition of the Eagle Ford Shale is divided into two different settings based on lithological changes: a western, carbonate-dominated setting and an eastern, clastic-dominated setting, separated by the San Marcos Arch (Denne et al., 2014).

According to Ewing (1987), a linear zone known as the Frio River Line (encompassing an area 10 mi x 100 mi) lies northeast of the Del Rio Fold Belt and passes through the southwest corner of Frio County and the Northeast corner of La Salle County (Ewing, 1987). Four major tectonic and structural events define this zone: a) normal fault zones to the northeast; b) the Laramide Fold to the southwest; c) the consequential Cretaceous igneous intrusions and volcanism; and d) a regional decollement zone supported by salt tectonics. Each of these influences is a sophisticated process by itself but together, they construct an extremely complicated geologic setting when considered with broader events (Ewing, 1987).

We first consider the major normal fault belts in this region. The Balcones Fault Belt and Luling Fault Belt strike from southwest to northeast, while the Charlotte Fault Belt (also known as the Charlotte-Jourdanton Fault Belt) strikes from southeast to northwest (Figure 2). Since the former two fault belts are spatially distant from our study area, this thesis will only discuss the Charlotte Fault Belt and its effects on the local Eagle Ford Shale. Historically, normal faulting in the Charlotte Fault Belt is thought to have started during the deposition of the Eagle Ford Shale (Upper Cretaceous) and continued through the Tertiary (Fowler, 1956). The subsequent crustal thinning induced volcanism primarily in Zavala County (west of the study area). Moreover, the relationship between normal faults and volcanism is contemporaneous instead of spatial (Fowler, 1956). The igneous activity in this region is exemplified by mainly disconnected basalt dikes and sills. Injection

of those basaltic sills allowed localized serpentinization to occur, which has been examined in the Eagle Ford Shale core samples. However, since the spatial occurrence of these serpentines are disjointed, little work has been done to correlate them. In terms of mineral composition, these volcanics are ultramafic, alkaline-rich, and silica-unsaturated (Ewing and Caran, 1982; Chakrabarti et al., 2008 Tedesco et al., 2010). Even though three major fault zones are present near the study area, there is no indication of a history of rift development or any rifting activities in process (Ewing, 1987). Consequently, understanding the actual roles of faults and igneous activities will help us interpret the chemical composition of the fluids in the Eagle Ford Shale and the thermal maturation of the Eagle Ford Shale.

Second, although Laramide folding around southwestern Texas during the uplift of the Rocky Mountains did not directly contribute to the formation of the Eagle Ford Shale, the Laramide orogenic belt did serve as the source for materials subsequently deposited on top of the Eagle Ford Shale and Austin Chalk (Ewing, 1987). These sediments increased burial depths of the Eagle Ford, and therefore thermal maturation of the Eagle Ford Shale (Ewing, 1987). For example, a major Laramide fold, known as the Chittim Anticline, is located at the northwest corner of the study area (Ewing, 1987). Folding near the Chittim Anticline led to deeper burial depths of the Eagle Ford Shale proximal to this formation (Ewing, 1987). Evaluations of the hydrocarbon thermal maturity along the hinge line of the anticline were compared to the maturity of the limbs of the anticline, and the results show higher values in the limbs (Cabot proprietary documents, 2014).

Finally, Ewing (1987) determined that salt tectonics did not play an important role in deposition of the Eagle Ford Shale. This conclusion was reached by citing the pinch out of a major salt unit (the Louann Salt) in the petroleum system on southeastern Texas, Louisiana, and the Gulf of Mexico prior to the deposition of the Eagle Ford Shale. The Louann Salt is discontinuous near

the origin of the normal faults, implying the tense impacts caused by salt tectonics (Ewing, 1987). Therefore, we will not discuss the local effects caused of salt tectonics in this thesis.

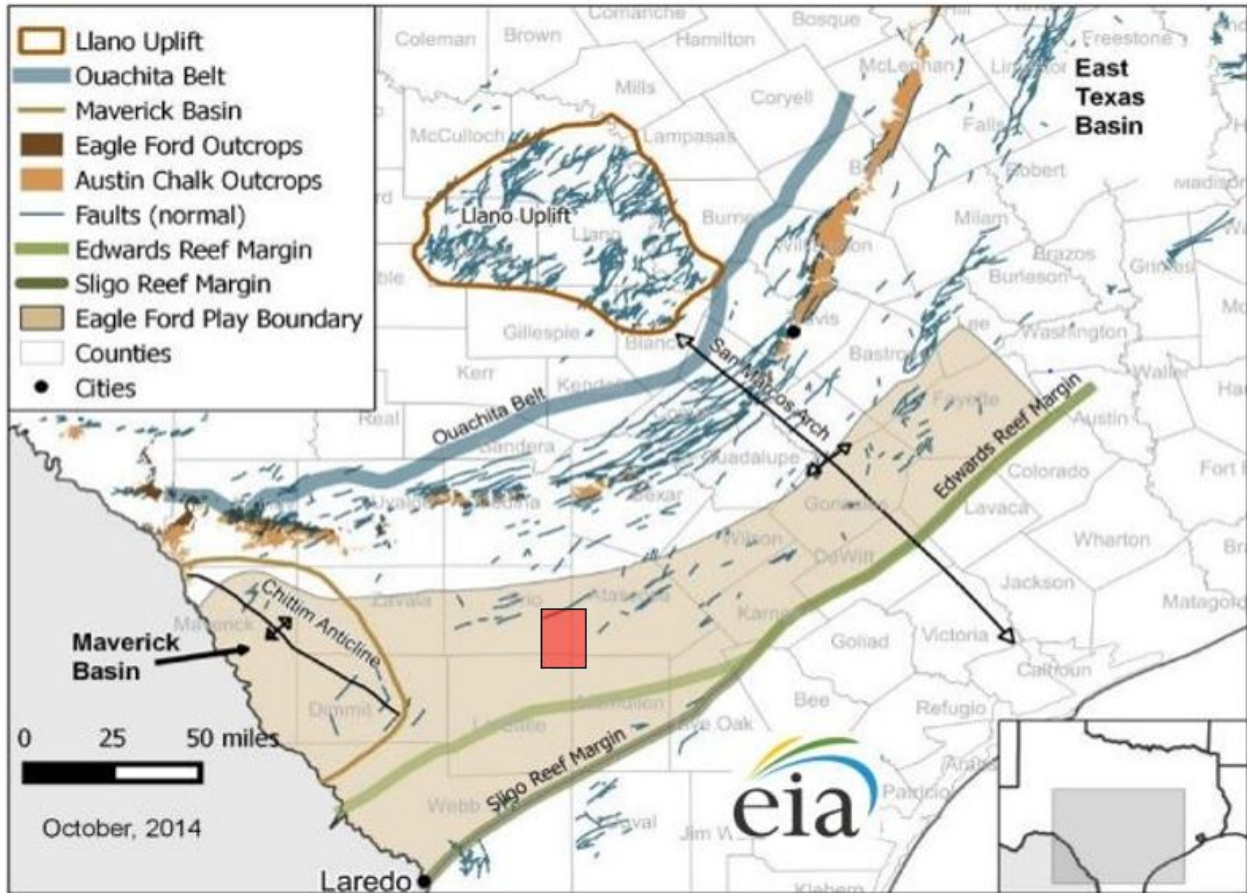


Figure 2. Map showing major regional structural and tectonic features around the Eagle Ford Play. Study area is represented by the red box (San Marcos Arch to the northeast, Maverick Basin to the west, Ouachita Belt to the north, and Sligo Reef Margin to the south) (U.S. Geological Survey, Condon and Dyman, 2006; Bureau of Economic Geology, Hentz and Ruppel, 2011).

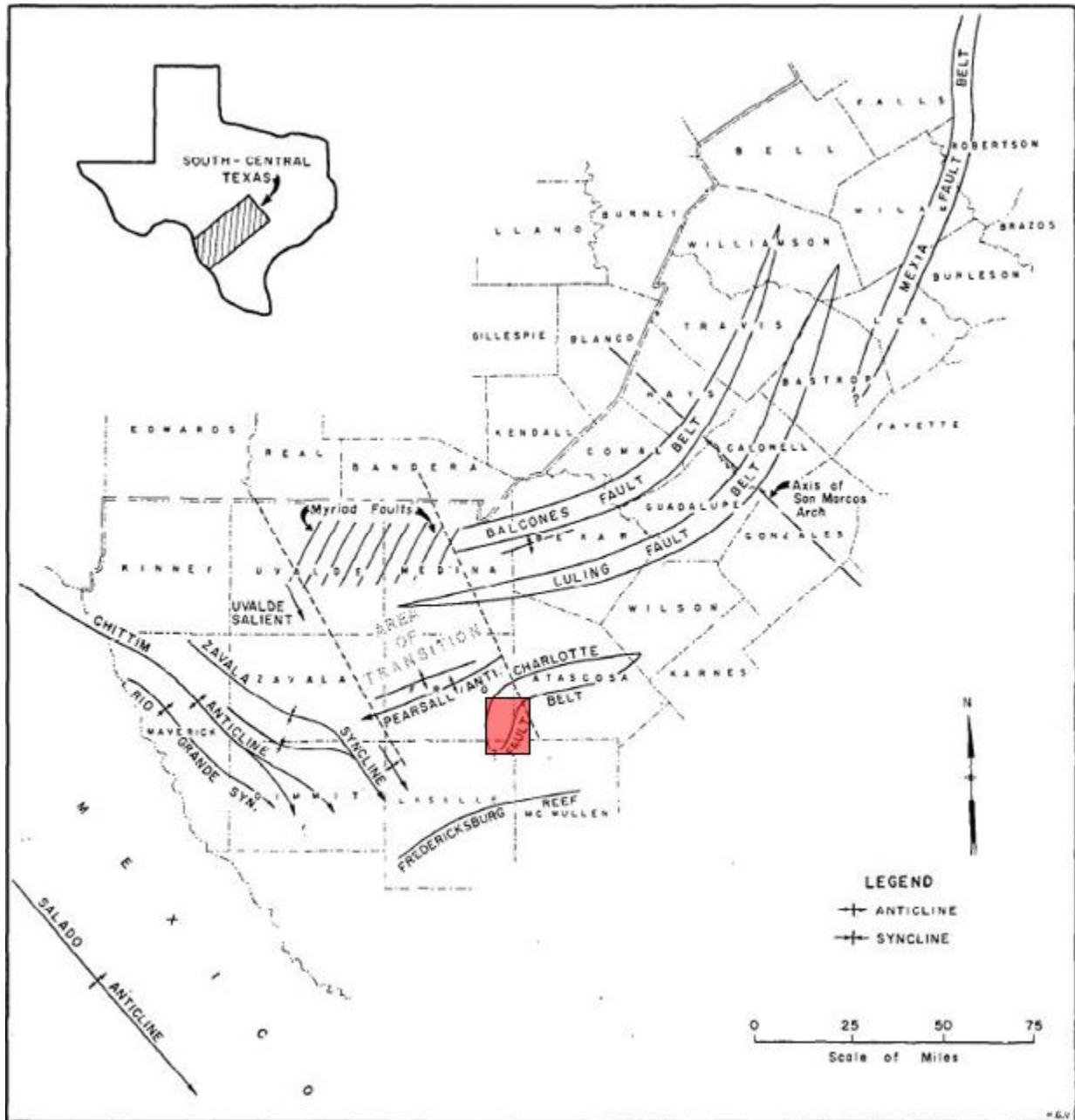


Figure 3. Map of major fault belts and folds in south-central Texas. Study area is represented by the red box (down-dip side of the Charlotte Fault Belt), with two parallel normal fault belts: Balcones and Luling Fault Belt to the north (figure from Fowler, 1956).

### Geochemical Background

We collected 27 oil and oil-associated gas samples from actively-producing oil and gas wells across the Atascosa, Frio, and La Salle Counties in Texas, United States in order to evaluate

hydrocarbon gas and fluid compositions related to the Eagle Ford Shale and to determine the thermal maturation of the study area. Previous work has been performed on the noble gas composition of the same samples (Harrington, 2015). All samples were analyzed for major gas composition (methane (CH<sub>4</sub> or C<sub>1</sub>), ethane (C<sub>2</sub>), propane (C<sub>3</sub>), butane (C<sub>4</sub>), pentane (C<sub>5</sub>), hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), oxygen (O<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), and nitrogen (N<sub>2</sub>)), and compound-specific stable carbon isotopic composition (C<sub>1</sub> to C<sub>5</sub> and CO<sub>2</sub>) following analytical standards (Hunt et al., 2012; Darrah et al., 2012 Darrah et al., 2014).

According to the composition of natural gases, they are generally classified into three groups: 1) dry gas, whose ethane (C<sub>2</sub>) or higher order hydrocarbons (C<sub>2+</sub>) content is less than 1%; 2) wet gas, which has more than 5% of C<sub>2</sub> and C<sub>2+</sub> hydrocarbons; and 3) intermediate gas, which has not been accurately defined but is commonly found in “deep” shales. We classify the natural gas type based on calculations of the molecular C<sub>2+</sub>/C<sub>1</sub> ratio for each sample from the Eagle Ford Shale.

Natural gas can be produced via biogenic (catalyzed by microbes) or thermogenic (induced by increasing temperature and pressure) processes (Tissot and Welte, 2012). Conventionally, the source of natural gas is determined based on the hydrocarbon molecular content (C<sub>1</sub>/C<sub>2+</sub> or C<sub>1</sub>/(C<sub>2</sub>+C<sub>3</sub>)) (commonly termed the Bernard parameter) and isotopic values of carbon (δ<sup>13</sup>C) and hydrogen (δ<sup>2</sup>H) in methane, ethane, propane, etc. (Tissot, 1978; Clayton, 1991; Rice and Claypool, 1981; Schoell, 1980, 1983; Whiticar et al., 1994).

Commercial natural gases are typically divided into two genetic groups by relatively atypical geochemical and stable carbon isotopic particularities (Clayton, 1991; Jenden and Kaplan, 1986; Rice and Claypool, 1981; Schoell, 1983; Whiticar et al., 1986). The first category is biogenic gases, which are also known as microbial or bacterial gases. This type of natural gas is normally produced from microbial degradation activity by anaerobic bacteria in shallow environments (< 3km burial depth)

with comparably low temperatures ( $< 100^{\circ}\text{C}$ ) (Machel, 2001). Other distinct characteristics of biogenic gases include low concentrations of  $\text{C}_2+$  hydrocarbons (low  $\text{C}_2+/\text{C}_1$ ) and isotopically light  $\text{C}_1$  ( $\delta^{13}\text{C}_1 < -60\text{‰}$ ) (Schoell, 1983).

Thermogenic hydrocarbons form from the thermocatalytic decomposition of kerogen with increasing temperatures associated with greater burial depths (i.e., termed catagenesis) (Tilley and Muehlenbachs, 2013; Tissot, 1978; Tissot and Welte, 1984; Whiticar et al., 1985). The hydrocarbon composition of thermogenic gases changes as the organic source (i.e., kerogen or liquid hydrocarbons) degrades. In general, there is a linear relationship between the stable C and H isotopes of various thermogenic natural gases. For example, there is an approximately linear relationship between the  $\delta^{13}\text{C}$  of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , etc. and thermal maturity, with enriched (i.e., heavier)  $\delta^{13}\text{C}$  resulting from an increase in thermal maturity (e.g., vitrinite reflectance or  $\text{R}_0$ ) (Whiticar et al., 1994). Similarly, as the thermal maturity of natural gases increases, the  $\text{C}_1/\text{C}_2+$  progressively increases (e.g., Schoell, 1980, 1983; Tissot and Welte, 1984; Whiticar et al., 1985).

Thermal maturity, defined as the degree of composition-altering reactions of organic matter driven by heat, constitutes a crucial characteristic of source rock during any successful exploration project. This feature is decidedly influenced by the highest temperature a unit has ever reached through its history rather than the present-day temperature. To acquire the greatest paleotemperature, two types of paleothermometers are generally utilized: chemical (e.g., Carbon Ratios, Rock-Eval, and Gas Chromatography) and biological (e.g., Spore Index, Vitrinite Reflectance ( $\text{R}_0$ ), and Conodont Alteration Index (CAI)) paleothermometers (Selley and Sonnenberg, 2016). In this case, no additional laboratory work was done and instead we employed an empirical relationship between stable carbon isotopic composition of  $\text{C}_1$  and  $\text{C}_2$  in natural gases and the vitrinite



reflectance of responsible source (initially established by Stahl and Koch (1974) and thereafter revised by Whiticar et al. (1984) and Faber (1987).

$$\delta^{13}\text{C}_1 (\text{‰}) = 15.4 \log_{(10)} \% R_o - 41.3, \quad (\text{I})$$

$$\delta^{13}\text{C}_2 (\text{‰}) = 22.6 \log_{(10)} \% R_o - 32.2. \quad (\text{II})$$

Since the Eagle Ford Shale contains Type II kerogen (Slatt et al., 2012), with low vitrinite reflectance ( $\% R_o \leq 0.5$ ), the formation will be determined as a thermally immature unit. Source rocks in oil-prone stage will show vitrinite reflectance between 0.5 and 1.2 while higher values of vitrinite reflectance ( $\% R_o$  ranges from 1.2 to 2.0) tend to be present in source rocks in gas-prone stage. If a source rock has undergone metagenesis, or carbon metamorphism, its vitrinite reflectance will be  $> 2.0$ .

## **METHODS**

### **Sampling**

Samples for this study were collected from 27 commercial producing oil and gas wells in Frio, Atascosa, and La Salle Counties in Texas with a depth range between 5,000 ft (1,524 m) to 8,000 ft (2,438 m) in the Eagle Ford Shale. We noted whether samples are associated or unassociated with faults.

### **Sample Analysis**

To prevent leaking and any possible chemical reactions between the oil and oil-associated gas samples and their transporting and storage accessories, samples were collected and stored in refrigeration-grade copper vessels which were flushed with at least 50 unit volumes of the same sample fluids as a preparation and then sealed with stainless steel clamps. After the samples arrived at the laboratory, the fluids were removed from the prepared copper vessel onto a vacuum line. The next step was to sonicate the extracted samples for about 30 minutes to ensure all dissolved gases were transferred from the mixed fluids.

Each sample was analyzed for two measurements: the major gas abundance ( $C_1$ ,  $C_2$ , hydrogen, oxygen, hydrogen sulfide, argon, and carbon dioxide) and the stable carbon isotopic composition based on the standard analytical methods (Hunt et al., 2012). To avoid obtaining stagnant fluids, all 27 wells had been in continuous, active production before sampling.

An SRS (Stanford Research System) quadrupole MS (Mass Spectrometer) was utilized to measure the major gas abundance in triplicate at The Ohio State University. According to the results of measuring referenced and cross-validated laboratory standards: 1) a synthetic natural gas sample offered by Praxair and 2) an atmospheric standard (in this case, Columbus air), daily values, after analyzing the external precisions standards, are: methane (0.95%), ethane (0.95%), nitrogen (1.25%),

carbon dioxide (1.50%), hydrogen (3.30%), oxygen (2.10%), and argon (0.95%). Standard analytical errors were no more than  $\pm 3.3\%$ .

## RESULTS

No marked air contamination was observed during the analysis of the 27 samples. For the major gas components, methane accounts for 0.116 to 0.672 ccSTP/cc, ethane ranges between 0.082 and 0.34 ccSTP/cc, while the concentration of carbon dioxide ranges from 0.0174 to 0.159 ccSTP/cc and hydrogen sulfide concentration ranges from 14.7 to 4980  $\mu$  ccSTP/cc (ppm) (Figure 4).

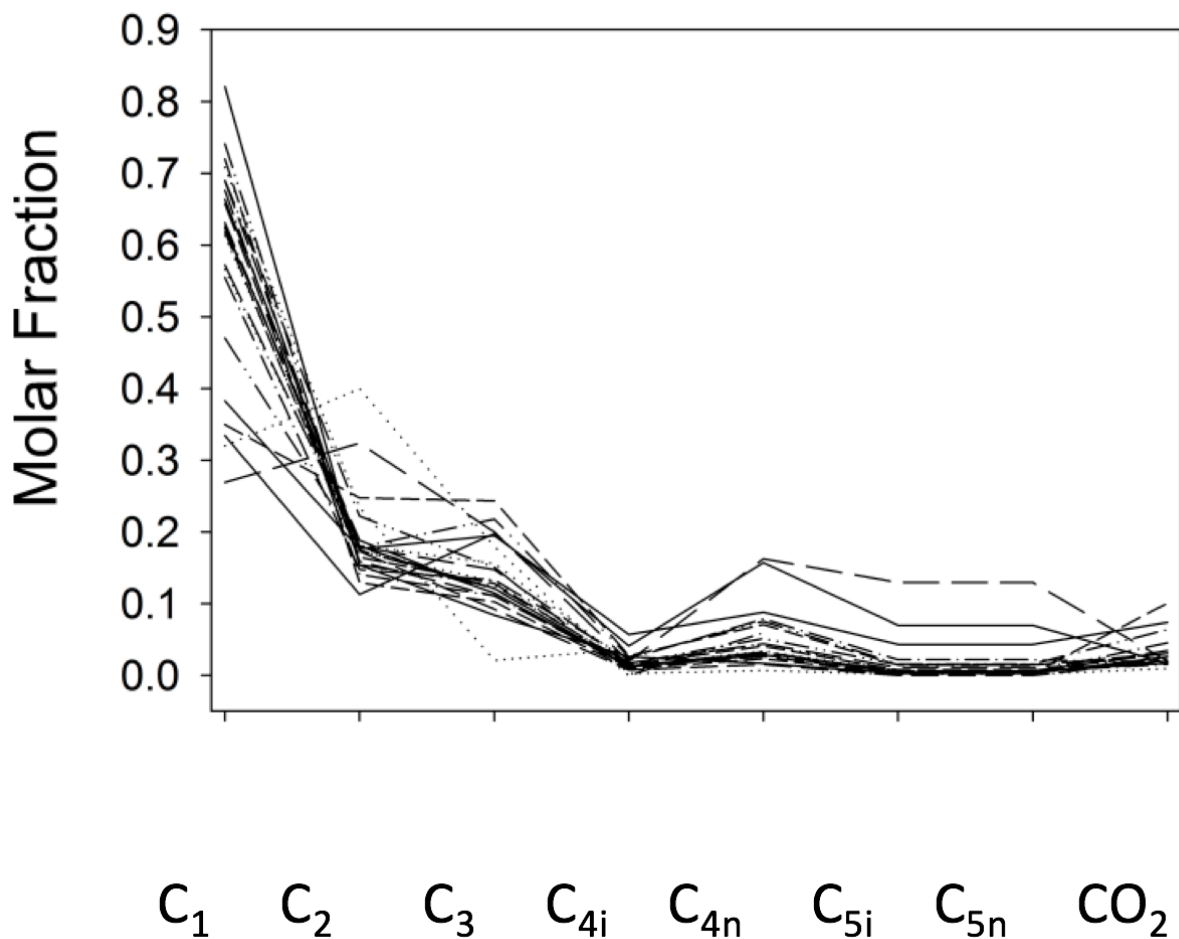


Figure 4. Plot shows that the major gas compositions of collected samples vary, however the general relationship indicates that these are dominantly wet and oil-associated natural gas.

Calculations of stable carbon isotopic composition were performed for all wells (Figure 5). The ratio of  $\delta^{13}\text{C}$  to methane ranges from -48.3 to -35.5 per million,  $\delta^{13}\text{C}\text{-C}_2\text{H}_6$  ranges from -36.7 to

-33.9 per million, and the values of vitrinite reflectance ( $\% R_o$ ) were calculated according to equations I and II, which range from 0.61 to 0.96 and fall into the oil prone window. The results show that the Eagle Ford Shale is mainly composed of thermogenic wet gas ( $0.11 \leq C_2+/C_1 \leq 1.4$ ), which can be further supported by interpretation of the early petroleum generation stage of the Eagle Ford Shale.

## DISCUSSION

All 27 samples collected and analyzed in this research confirm that the natural gases in the Eagle Ford Shale are in an early stage of thermal maturity (Schoell, 1980), commonly termed oil-associated (Jenden et al., 1993). Typically, oil-associated natural gases are considered as wet gas due to the molecular  $C_2+/C_1$  ratios exceeding 0.03 ( $> 3\%$  of the natural gases are ethane or other higher order aliphatic hydrocarbons). Among these samples, values of  $C_2+/C_1$  vary between 0.11 and 1.4, which are infrequently observed in many other geological settings. On the other hand, high concentrations of ethane and heavier aliphatic hydrocarbons indicate a thermogenic origin of the natural gases in the Eagle Ford Shale.

The stable carbon isotopic composition of methane ranges from -48 to -36 per mil, also suggestive of a thermogenic origin. Natural gases with a biogenic origin have much lighter values ( $\delta^{13}C_1$  (‰)  $\sim -60$  per mil) because of the microbial preference for  $^{12}C$  (Schoell, 1983). The stable carbon isotopic composition of ethane ( $\delta^{13}C_2$  (‰) ranges from -36.7 to -33.9) shows consistency with a thermogenic origin. In terms of each sample, the value of  $\delta^{13}C_1$  (‰) is always smaller than that of  $\delta^{13}C_2$  (‰), and on average, the difference between  $\delta^{13}C_1$  (‰) and  $\delta^{13}C_2$  (‰) is about 8 (Figure 5). According to Silverman (1971), this result indicates that hydrocarbon gases in the Eagle Ford Shale are oil associated.

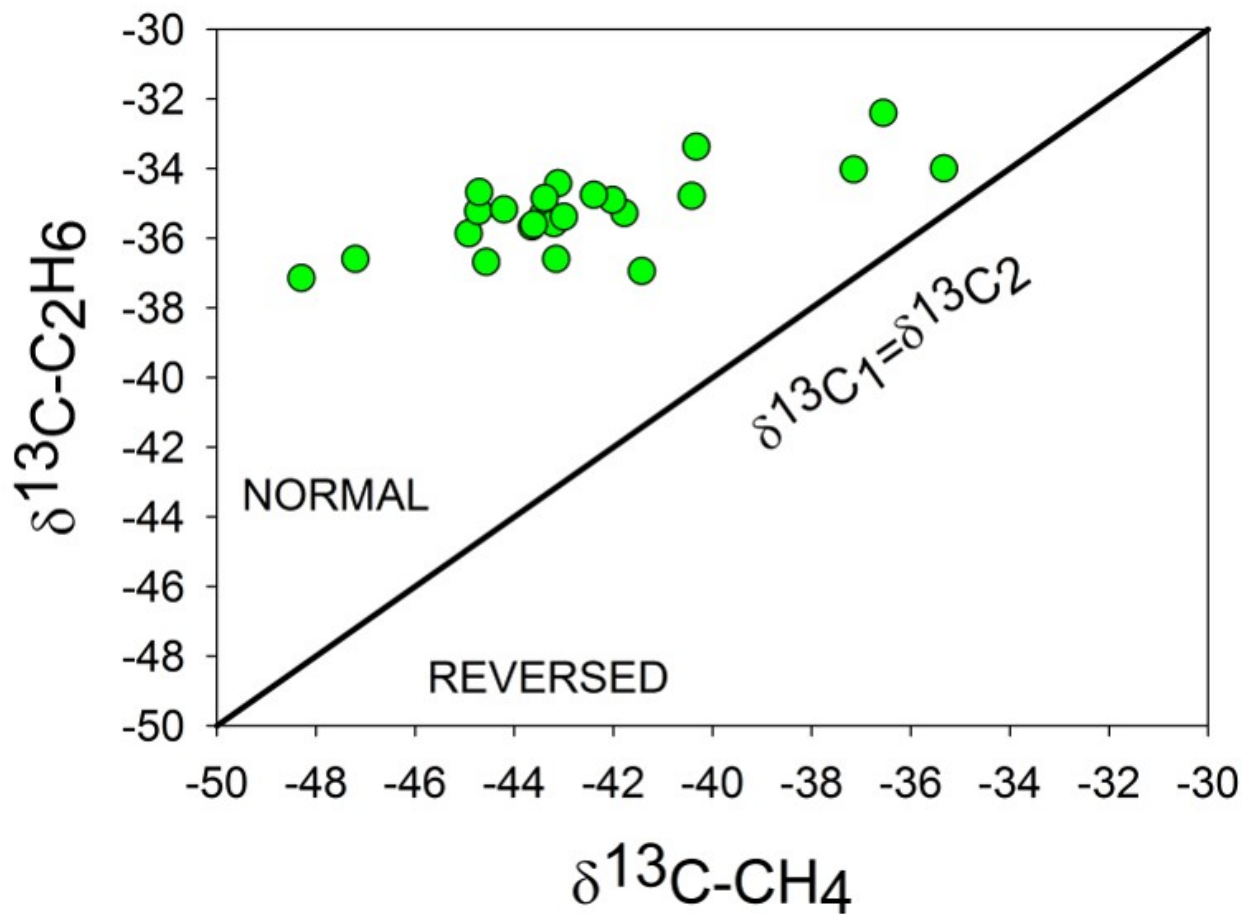


Figure 5. Cross-Plot of  $\delta^{13}\text{C}$  to methane and  $\delta^{13}\text{C}$  to ethane shows that all samples are in the normal range and no isotope reversals are present.  $\delta^{13}\text{C}_1$  values range from -48.3 to -35.5 per million with the average of data are around -42 per million, and  $\delta^{13}\text{C}_2$  values range from -36.7 to -33.9 per million with the majority of data are about -36 per million.

We provide two possible explanations for natural gases which are rich in ethane and heavier aliphatic hydrocarbons. We can classify these natural gases as either: 1) hydrocarbon gases generated by early stage thermal catalysis of liquid oil or 2) hydrocarbon gases generated from metagenesis. Since vitrinite reflectance has been calculated based on Equations I and II, the %  $R_o$  values computed from  $\delta^{13}\text{C}_1$  (‰) range between 0.4 and 2.4, with an average of 0.7, and the %  $R_o$  values

calculated from  $\delta^{13}\text{C}_2$  (‰) range from 0.6 to 1.0. These  $R_o$  values are consistent with oil generation and oil cracking window (Pawlewicz et al., 2005).

To further investigate the origin of hydrocarbon gases of the Eagle Ford Shale, a theoretical equation (Equation III) developed by Chung et al. (1988) was used to examine the relationships of compound-specific isotopes and determine if natural gas is generated by single or multiple processes and we have employed it to results of stable carbon isotope ratios of samples collected for this study:

$$\delta C_n = -1/n (\delta C_p - \delta C_m) + \delta C_p \quad \text{(III)}$$

In this equation,  $C_n$  are the numbers of carbon atoms in each hydrocarbon molecules,  $C_m$  represents the chemical bond between  $C_n$  and other carbons in the same kerogen molecule, and  $C_p$  define all other carbon atoms in that molecule (Chung et al., 1988). Figure 6 is a cross-plot (Chung Plot) of carbon isotope ratios of major hydrocarbon gases (methane, ethane, propane, and etc.) and their corresponding inverse carbon numbers of molecules resulting from plot  $\delta C_n$  as a function of  $1/n$ . Therefore, the slopes of lines in this plot are the isotopic fractionations in hydrocarbon gases generation stage ( $\delta C_p - \delta C_m$ ) and the y-intercepts represent the carbon isotope ratios of the heaviest molecules generated during kerogen thermal degradation (Chung et al., 1988).

The overall sublinear relationships with minor deviations in details of all samples indicate aliphatic hydrocarbons are generated at early stages of thermogenic maturation. Moreover, the close fit of the majority of all samples reflects a single stage of thermal maturity (Chung et al., 1988; James, 1983). In general, certain trends for methane and heavier gaseous hydrocarbons (n-butane and n-pentane) show deviations from the average slope. First, potential reasons for deviations for methane include multiple generations of hydrocarbon formation, chemical oxidation, or mixing with hydrocarbons from biogenic origin. Second, structural differences and isotopic heterogeneous



property might be responsible for deviations for n-butane and n-pentane. To understand these deviations more thoroughly, additional work is necessary.

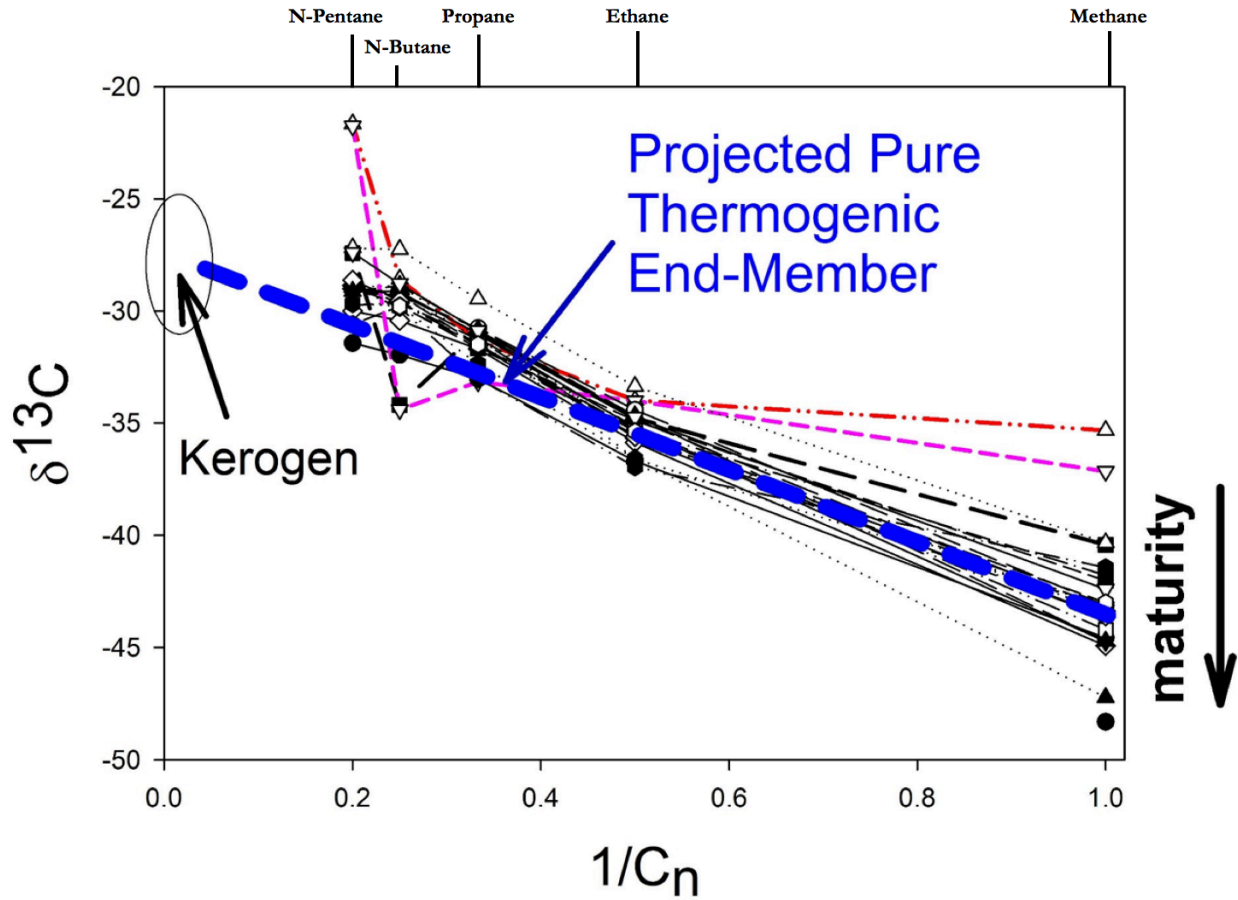


Figure 6. Cross-Plot of carbon isotope ratios of major hydrocarbon gases (methane, ethane, propane, and etc.) and their inverse carbon numbers of molecules (called a Chung Plot).

## CONCLUSIONS

To determine the composition, thermal maturity, and origin of the hydrocarbon gases of the Eagle Ford Shale, major gas composition, stable carbon isotope ratios, and relevant calculations of vitrinite reflectance were measured from collected samples. Results of major gas composition ( $0.11 \leq C_2+/C_1 \leq 1.4$ ) suggest that natural gas of the Eagle Ford Shale is thermogenic and oil-associated wet gas, which is further supported by the distribution of stable carbon isotope ratios of methane and ethane (values of  $\delta^{13}\text{C}-\text{CH}_4$  are always smaller than those of  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$ ). Moreover,  $R_o$  values calculated from stable carbon isotope ratios of methane ( $\delta^{13}\text{C}-\text{CH}_4$  range from -48 to -36 per mil) and ethane ( $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  ranges from -38 to -32 per mil) imply an early stage in oil window thermal maturity. The system has not reached sufficient thermal maturity to generate dry natural gas or undergo metagenesis and this is evidenced by the occurrence of only “normal” isotopic trends and no isotopic reversals. Further, the linear nature of the Chung Plot suggests that the majority of hydrocarbons are generated in a single stage of thermal maturity, suggesting that burial of the basin has likely stalled.

## **RECOMMENDATIONS FOR FUTURE WORK**

More specific information about Eagle Ford Shale fluids can be obtained in a number of ways. In order to resolve the origins, degree of degradation of fluids, and most importantly, to determine the cause of C<sub>2+</sub> enrichment of natural gases which has not yet been conclusively determined by vitrinite reflectance, more hydrocarbon data should be collected and analyzed for compound-specific isotopes in order to learn more about the Eagle Ford Shale. The Chung Plot can also be expanded to make more evaluations regarding the deviations of heavier gaseous hydrocarbons (butane and pentane). Finally, samples of the Eagle Ford Shale in other study areas should be collected and analyzed along with samples of other formations at the same locations of this study to understand more about the context and properties of the Eagle Ford Shale.

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